EXHIBIT 11

ENVIRONMENTAL FORENSICS
2020, VOL. 21, NO. 1, 99–112
https://doi.org/10.1080/15275922.2019.1694098

Taylor & Francis
Taylor & Francis Group

Check for updates

Sources of polychlorinated biphenyl blank contamination and their impact on fingerprinting

Lisa A. Rodenburg[a], Michael R. Hermanson[b], and Amy L. Sumner[b]

[a]Department of Environmental Sciences, Rutgers University, New Brunswick, NJ, USA; [b]Spokane County Environmental Services, Spokane, WA, USA

ABSTRACT
The development of high-resolution mass spectrometry methods for the measurement of polychlorinated biphenyls (PCBs) in environmental samples has dramatically reduced detection limits, leading to problems obtaining clean blanks. When PCBs are detected in samples at concentrations similar to the blanks, blank contamination must be addressed before fingerprinting and source apportionment through positive matrix factorization (PMF) can be successful. We tested a variety of blank correction methods using data from a study of water column concentrations of PCBs in the Spokane River, where concentrations of Σ_{209}PCBs in whole water samples averaged 171 pg/L without blank correction and Σ_{209}PCBs in the blanks averaged 88 pg/L. The results suggest that subtracting blank masses from sample masses can lead to erroneous results. Instead, censoring at one times the batch-specific blank level is a better approach. The sources of PCBs in field and method blanks were investigated by examining their congener profiles via PMF. The results suggest that commercial PCB formulations (in the US, Aroclors) continue to be the primary source of PCBs in blanks forty years after PCB production and use were banned in the United States. Other sources of PCBs to blanks include PCB 11 from pigments; PCBs 44 + 47 + 65, 45 + 51, and 68 arising from polymers cured using bis(2,4-dichlorobenzoyl) peroxide; and PCBs 1, 2, 3, 4, 8, 15 and others arising from silicone products derived from phenylsiloxanes, such as silicone-based adhesives.

KEYWORDS
PCB; blank contamination; silicone; siloxanes; Aroclor; factor analysis; positive matrix factorization

Introduction

Polychlorinated biphenyls (PCBs) are persistent, toxic, bioaccumulative chemicals (Agency for Toxic Substances and Disease Registry [ATSDR], 2000) that were banned in the United States under the Toxic Substances Control Act in the 1970s, and are banned internationally under the Stockholm Convention on Persistent Organic Pollutants (United Nations Environment Program, 2001). PCB manufacture began in the United States in the 1930s and reached its peak in the 1970s just before the ban (ATSDR, 2000). PCBs were detected in biota in the 1970s, prompting regulatory action (Hetling et al., 1978). Since that time, methods to measure PCBs in environmental samples have grown ever more sophisticated, with decreasing detection limits and increasing resolution of individual PCB congeners. In 1999, the U.S. Environmental Protection Agency (EPA) promulgated method 1668 (US EPA, 1999), which measures all 209 PCB congeners in environmental samples using high-resolution mass spectrometry, allowing detection limits on the order of 0.2 pg/L in water. Given these low detection limits, PCBs are routinely detected in quality control samples, including field, travel, and method blanks.

The Spokane River is on the State of Washington's 303(d) list for impairment by PCB contamination. The impairment is based on concentrations of PCBs in fish tissue that exceed a fish tissue equivalent concentration for applicable water quality standards (LimnoTech, 2016). In the data set considered here, Σ_{209}PCBs were detected in samples of whole water from the Spokane River at an average concentration of 171 pg/L (without blank correction) with an average of 88 pg/L found in the blanks (for this calculation, non-detects were assumed to equal zero concentration). Although low, these concentrations exceed the prevailing water quality standard (WQS) for PCBs in

CONTACT Lisa A. Rodenburg rodenburg@envsci.rutgers.edu Department of Environmental Sciences, Rutgers University, 14 College Farm Road, New Brunswick, NJ 08901, USA

Supplemental data for this article is available online at https://doi.org/10.1080/15275922.2019.1694098

the State of Washington of 7 pg/L. The Spokane Tribe of Indians has a WQS of 1.34 pg/L (LimnoTech, 2016). PCB loads to the river must therefore be reduced before the WQS can be achieved.

In order to reduce loads, it is necessary to determine the primary sources of PCBs to the river. Several attempts have been made to quantify these loads. One approach is to conduct a fingerprinting analysis on PCBs in the river in order to apportion sources, but this is complicated by the presence of significant PCB levels in the blanks. How should blank contamination be addressed when conducting source apportionment via factor analysis? A literature search found no published papers that address this issue. The user's guides for the various positive matrix factorization (PMF) software versions contain no mention of blank contamination (Paatero, 2000; Norris et al., 2009; Norris et al., 2014). The impact of blanks contaminated with organic carbon on source apportionment of aerosols has been investigated (Kim et al., 2005; Zhao et al., 2006). These studies have suggested that blank concentrations should be subtracted from measured concentrations, with the corrected concentrations submitted for factor analysis. However, some EPA guidelines suggest that blank subtraction is not recommended. For example, EPA method 8270 D (US EPA, 2014) for measurement of semivolatiles by gas chromatography/mass spectrometry states that "The laboratory should not subtract the results of the [method blank] from those of any associated samples. Such "blank subtraction" may lead to negative sample results."

It is important to note that the procedure for handling blank contamination might be different depending on how the data are to be used. For example, guidance from Washington State (Department of Ecology, State of Washington, 2018) states that "the choice of a censoring technique and factor (e.g. 3×, 5× or 10×) is specific to data, project needs, and the study objective. For comparison, blank censoring at 3× or 5× is used for identification of sources and can be a semi-quantitative analysis that may yield false positives which prevents it from being useful for the purpose of determining reasonable potential." In their Hazard Ranking System Guidance Manual, EPA states that, for purposes of establishing a release of a chemical, the concentration detected in the release sample should be compared to background: "If the background level is greater than or equal to its DL, the minimum requirement for an observed release is that the concentration in the release sample is at least three times greater than the background level" (US EPA, 1992). The procedure for dealing with blank contamination might be different when the data are to be used for fingerprinting and source apportionment, as in the present work, but to our knowledge, there is no specific guidance from EPA concerning blank correction in such scenarios.

Method 1668 (US EPA, 1999), which was used for PCB analysis in the study considered here, states that the "recommended procedure for blank correction … is that a result is significantly above the blank level, and the level in the blank may be subtracted, if the result is greater than the mean plus 2 standard deviations of results of analyses of 10 or more blanks for a sample medium," citing Ferrario et al. (1997), who specifically discuss the difficulties associated with obtaining low or zero concentrations of PCBs in blanks when using high resolution mass spectrometry. These authors note that blank contamination frequently consists of Aroclor-type congeners. However, in our experience, non-Aroclor congeners are frequently abundant in blanks as well.

The purpose of this study was to identify an approach to blank correction that yields meaningful and interpretable results from the fingerprinting of PCB sources in the Spokane River. In order to do this, it was also necessary to identify the types of PCB sources that impact the blanks.

Methods

Study location

The Spokane River runs approximately westward for 180 km from its source at Lake Coeur d'Alene in Idaho to its confluence with the Columbia River in Washington State (Figure 1). During this course, it flows through the city of Spokane, WA and thence forms the southern boundary of the reservation of the Spokane Tribe of Indians. The watershed covers about 15,500 km^2 of various land uses, including developed, forested, and agricultural lands. The total population for the watershed is estimated to be about 570,000 (LimnoTech, 2016). Potential sources of PCBs to the river include two industrial and six municipal water treatment facilities, stormwater runoff, and groundwater known to be impacted by PCBs (LimnoTech, 2016).

The hydrology of the Spokane River is characterized by relatively low flows in the summer and high flows during the spring freshet. During the summer months, flow is also regulated by the Post Falls Dam which forms the outlet of Coeur d'Alene Lake (LimnoTech, 2016). The River also receives large

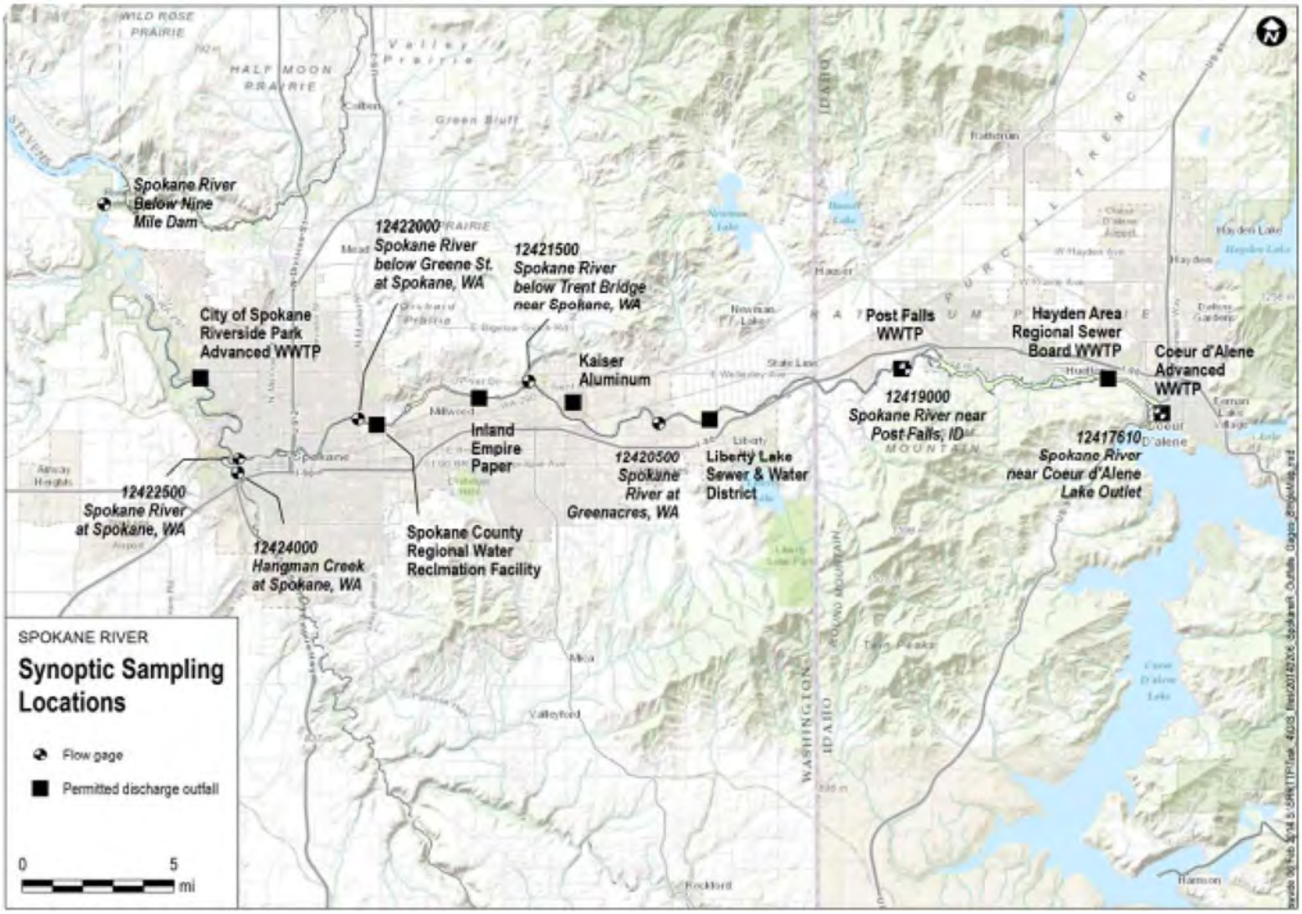

Figure 1. Map of the study area, from LimnoTech (2015). The sampling stations are abbreviated as follows: HC1 = 12424000 Hangman Creek, SR1 = below Nine Mile Dam, SR3 = 12422500 at Spokane, SR4 = 12422000 Greene Street, SR7 = 12421500 Trent Bridge, SR9 = 12420500 Greenacres, SR12 = 12419000 Post Falls, SR15 = 12417610 Coeur d'Alene outlet. Not shown on this map, SR8a was an in-river station at the Kaiser Aluminum plant.

inflows of groundwater. On average, the Spokane River and aquifer exchange 1,579 cubic feet per second as the river travels from Lake Coeur d'Alene to the Nine Mile Dam. During the summer months over 80 percent of the flow at Nine Mile Dam (downstream limit of the study area; see Figure 1) is from inflows from the aquifer (Hsieh et al., 2007).

Sample collection

Sampling and analysis were conducted under a Sampling and Analysis Plan (SAP) and a Quality Assurance Project Plan (QAPP) prepared by LimnoTech for the Spokane River Regional Toxics Task Force (SRRTTF) (LimnoTech, 2014a, 2014b). Whole water grab samples for PCB analysis (2.36 L) were collected in amber glass bottles by direct immersion in the river leaving no headspace. Samples were stored at 4 °C until extraction. PCBs were analyzed via EPA method 1668 C by SGS AXYS (Sidney BC Canada). Additional quality assurance data are provided in supporting information. Field blanks were prepared by the contract laboratory and traveled with the sampling media (in this case, amber glass bottles). They were collected at a frequency of 10% or one blank per sampling event. A method blank was described in the QAPP as an "analyte free matrix", i.e. HPLC grade water, prepared and analyzed by the contract laboratory. One method blank was analyzed for each sample batch. Extraordinary care was taken to obtain the cleanest blanks possible. As a result, the average Σ_{209}PCB concentration in the blanks of 88 pg/L was low compared to other studies. For comparison, water blanks from the Contamination Assessment and Reduction Project, which were also analyzed by SGS AXYS, averaged 852 pg/L Σ_{209}PCBs (Contamination Assessment and Reduction Project [CARP], 2007). Thus in the case of the Spokane River, the blank problem arises because of low ambient PCB concentrations in the water column and small sample volumes (2 L) and not because of high blank levels.

The Spokane River ambient water data set analyzed here included 139 Spokane River water column

samples (listed in supporting information Table S-3) collected in conjunction with the SRRTTF 2014 synoptic sampling, 2015 synoptic sampling and the 2016 monthly sampling. Duplicate samples were not averaged, but entered into the PMF input as two separate samples.

Analysis of the 42 congeners routinely detected in the 48 blanks via PMF resulted in a model solution in which many congeners, including PCBs 68 and 209 (which are likely to arise from inadvertent PCB sources) were not well described, i.e. the agreement between the model predicted concentrations and the measured concentrations was poor ($R^2 < 0.2$). Therefore, in order to have enough blank data for a more meaningful PMF analysis, the blank PCB data input included the 48 blanks from the ambient water study plus 114 blanks associated with a different study in the Spokane River watershed that was conducted over the same time frame and used the same contract laboratory for sample analysis as the surface water sampling (Spokane County Water Reclamantion, 2015). See supporting information for details of the blanks collected under this study.

In all cases, all 209 PCB congeners were measured in 159 peaks using the SPB-octyl gas chromatography column. Each peak represented between one and six coeluting PCB congeners. In the present work, the different permutations of this data set that were analyzed using PMF included between 73 and 59 of these peaks. The remaining peaks were not included because they were too often flagged as non-detect (ND) under the various blank correction schemes described below. Table S-1 of supporting information shows which peaks were included in each model, and also shows all co-elutions.

Two different types of blank samples from the ambient water study were utilized in this analysis: Batch specific method blanks that are analyzed during the same batch as the sample, and associated field blanks which refers to the field blank collected on the same day as the sample. The associated field blank was often but not always analyzed in the same batch as the sample. These blanks were used two ways: 1. The more aggressive approach as to use the maximum value on a per congener basis of the batch specific method blank and associated field blank. 2. The less aggressive approach used the measured value of the congener-specific concentration in the method blank. In most instances there is only one method blank, but there are some instances where the lab analyzed three method blanks with each batch. In those cases, the average of the three method blanks on per congener basis was used to represent the batch specific method blank.

PMF analysis

PMF is an advanced factor analysis method developed by Paatero and Tapper (1994). All factor analysis techniques, including PMF and principle components analysis (PCA), define the sample matrix as a product of two unknown factor matrices with a residue matrix:

$$X = GF + E \tag{1}$$

The sample matrix (X) is composed of "n" observed samples and "m" chemical species. "F" is a matrix of chemical profiles of "p" factors or sources. The "G" matrix describes the contribution of each factor to any given sample, while "E" is the matrix of residuals. The PMF solution (i.e., "G" and "F" matrices) is obtained by minimizing the objective function "Q" through the iterative algorithm:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} (e_{ij}/s_{ij})^2 \tag{2}$$

The calculated "Q" is the sum of the squares of the difference (e_{ij}) between the observations (X) and the model (GF), weighted by the measurement uncertainties (s_{ij}). As a result, lower calculated "Q" values are desirable as they indicate a better fit to the input data (Polissar and Hopke, 2001).

PMF analysis of any data set therefore yields two matrices: the F matrix, which consists of the fingerprints of the factors, and the G matrix, which consists of the concentration of each factor in each sample (in the same units used in the input data set). The success of the various blank correction schemes was evaluated primarily by examining the F matrix. Specifically, success was judged based on whether the PMF model converged on a stable solution, and whether it produced fingerprints (F matrix) that resemble known PCB sources.

Full details of the methods used to construct the PMF input matrixes, run the PMF model, choose the optimal number of factors, and evaluate the output are given in Rodenburg and Leidos (2017) and are briefly summarized here.

The PMF2 software was used for this examination because more recent versions of PMF developed by the USEPA have been shown to perform poorly for PCB data (Rodenburg and Meng, 2013; Rodenburg et al., 2015b; Rodenburg and Delistraty, 2019). The PMF2 program requires three input data sets: concentration, limits of detection (LOD), and uncertainty. All three of these inputs have the same dimensions, i.e. the same number of peaks and samples.

- Concentration matrix: When analyte concentrations were designated as ND, they were replaced with a

random proxy value between 1 and 100 percent of the limit of detection (LOD), which in this case was the method detection limit provided by the contract lab. In order to eliminate this proxy value as a confounding variable, a set of proxy values was generated that was used for all permutations of the data set described above, i.e. the exact value of this random proxy did not change from one data set to the next. A further discussion of the treatment of non-detects is provided in supporting information.

- LOD matrix: method detection limits were used as provided for all data points.
- Uncertainty matrix: As in previous analysis of EPA Method 1668 data (Du et al., 2008; Rodenburg et al., 2011; Praipipat et al., 2013; Rodenburg and Meng, 2013; Rodenburg et al., 2015a), the relative standard deviation of the surrogate recoveries (RSDSR) was used as the uncertainty. These generally range from approximately 10 to 15%.

When constructing these input data sets, it is necessary to exercise judgement about which peaks to include and which to exclude. For the present work, PCB peaks were included when the peak was designated as detected in at least half of the 139 samples. The data set of PCB concentrations in the blanks violated this rule out of necessity: it included congeners that were detected in at least 68 of the 162 blanks (not to be confused with the 139 *samples*).

Throughout this report, we have indicated how much of the total mass of all 209 PCB congeners detected in all samples (i.e. as reported by the contract lab) was included in each permutation of the data set (Table 1). This percentage ranges from 96.6% in the uncorrected data set with 73 peaks (Uncor73) to just 51.4% in the data set generated from blank subtraction using the maximum concentration detected across all blanks and excluding peaks $44+47+65$ and $45+51$ (MaxSub59). One of the goals of this study was to determine which combination of approaches to blank correction is best for analysis of the data by PMF. One of the criteria used to make this determination was that the approach should retain as much of the PCB mass as possible.

Construction of PMF inputs

We analyzed several permutations of the ambient water data set with the following modifications:

- Approach A: No blank correction. Interpret the output of the model with the assumption that one or more of the resolved factors may represent

Table 1. Summary of the data sets analyzed by PMF and their results. "Low MW Aroclors" refers to Aroclors 1016, 1242, and 1248.

										Distribution of PCB mass				
Name	Correction method	Which blanks?	Max or average?	Peaks	Congeners	% of PCB mass included	# factors	Silicone factor?	Unidentified factor?	Low MW Aroclors	Aroclor 1254	Aroclor 1260	PCB 11 factor	Other
Uncor73	None	None	NA	73	117	96.6%	6	Mono & tetra	no	32%	25%	16%	17%	11%
Uncor68	None	None	NA	68	112	94.4%	7	Tetra	no	46%	21%	15%	14%	5%
Uncor61	None	None	NA	61	103	90.9%	7	Tetra	no	45%	21%	15%	13%	6%
Uncor59	None	None	NA	59	98	85.2%	6	None	no	47%	22%	15%	15%	0%
BatchCensor68	Censor	Batch	Average	68	112	90.7%	5	None	no	41%	24%	23%	12%	0%
BatchCensor61	Censor	Batch	Average	61	103	87.7%	7	Tetra	no	47%	16%	20%	10%	7%
BatchSub68	Subtract	Batch	Average	68	112	68.3%	6	None	no	51%	22%	19%	8%	0%
BatchSub61	Subtract	Batch	Average	61	103	66.4%	5	None	no	43%	25%	22%	10%	0%
MaxCensor61	Censor	All	Max	61	103	78.9%	5	None	no	47%	21%	19%	13%	0%
MaxCensor59	Censor	All	Max	59	98	74.2%	5	None	no	45%	21%	21%	13%	0%
MaxSub61	Subtract	All	Max	61	103	54.2%	6	None	yes	37%	23%	25%	9%	5%
MaxSub59	Subtract	All	Max	59	98	51.4%	6	None	yes	38%	25%	19%	10%	8%

blank contamination. These model runs are labeled "Uncor."

- Approach B: Censor (exclude) concentrations of peaks that were present in the method blanks. We initially intended to censor concentrations that are within 3 times, 5 times, and 10 times the blank level. The results of this approach left too few congeners with enough data above the censor limit to construct a useful PMF model. Therefore, we also investigated censoring at one time (1x) the blank level. Censored concentrations were designated as ND and therefore assigned a proxy value between zero and the detection limit and assigned a higher uncertainty in the PMF model. Two sets of values were used for the censoring: either the batch-specific blank concentrations (approach 2 above; these runs are called "BatchCensor") or the maximum of all blank concentrations (approach 1 above; called "MaxCensor").
- Approach C: Subtract blank masses from sample masses. When such a subtraction resulted in a zero or negative concentration, the data point was designated as ND. As with the censoring, two sets of values were used: the batch-specific blank concentrations (these runs are called "BatchSub") or the maximum of all blank concentrations (called "MaxSub").
- Approach D: Exclude from the PMF2 analysis specific congeners that are often present in the blanks. This may underestimate the importance of non-Aroclor sources in the Spokane River. These runs are identified by the number of peaks included in each run, which is the number appended at the end of each data set label (for example, Uncor73 is a data set that was not corrected for blanks and included 73 peaks). Runs with 59 peaks excluded PCBs 44 + 47 + 65, and 45 + 51. PCB 68 was never included in any of the surface water data sets analyzed because it was not detected in enough samples, but it was included in the blank data set because it is known to be associated with certain non-Aroclor PCB sources (Perdih and Jan, 1994).

We analyzed Spokane River ambient water column data by the above approaches and compared the various model outputs to determine which approach (or combination of approaches) yielded the most useful information about PCB sources to the river.

Results

PMF results from the blank data set

Before analyzing the ambient water data, the blanks themselves were analyzed via PMF. In the blanks from the ambient water study, the field blanks contained an average of 130 pg/L Σ_{209}PCBs (ranging from 30 to 1064 pg/L) and the method blanks contained an average of 56 pg/L Σ_{209}PCBs, ranging from 0 pg/L (no detections) to 239 pg/L. The blanks from the other study contained an average of 168 pg/L Σ_{209}PCBs (ranging from 23 to 768 pg/L). PCB concentrations in the blanks from the ambient water study were approximately log normally distributed (median = 60 pg/L, skewness = 6.1). (In all of these calculations, non-detects were set to zero.) The blank with the highest PCB concentration was an ambient study field blank from August 12, 2014, in which the Σ_{209}PCB concentration was 1064 pg/L whereas the next highest field blank concentration in the ambient study was 138 pg/L. When this outlier is excluded from the comparison, field blanks from the ambient water study have higher concentrations (average = 85 pg/L) than method blanks from the same study (average = 56 pg/L) (two-tailed t test with unequal variances; $p < 0.05$).

The PMF analysis of these blanks included 42 peaks comprising 75 congeners. These 42 peaks contained 90% of the PCB mass detected in all 159 peaks/209 congeners, i.e. the discarded congeners contained just 10% of the mass. In the blank input, 27% of the data points were designated as ND.

The optimal solution for the blank data set contained seven factors (shown in supporting information Figure S-1). Four of the seven factors resemble the Aroclor PCB formulations produced in the United States by Monsanto and analyzed by Rushneck et al. (2004). The three remaining factors represent non-Aroclor PCBs, i.e. PCBs arising from inadvertent production during other chemical processes. One factor was dominated by PCB 11, with this one congener explaining 77% of the fingerprint. It arises from the use of pigments, especially the diarylide yellow pigments (Litten et al., 2002; The Japanese Ministry of Economy Trade and Industry [METI], 2012, 2014). Another factor contained PCBs 68 (2.9% of the fingerprint) as well as PCBs 44 + 47 + 65 (59%), 45 + 51 (12%), and 20 + 28 (4.0%). This fingerprint will be called the "peroxide" factor because it is thought to arise from polymers that are produced using bis(2,4-dichlorobenzoyl) peroxide as a cross-linking agent. These congeners PCBs have been found in silicone rubber (Perdih and Jan, 1994). More recently, Herkert et al. (2018) have suggested that these congeners can come from polyester resins cured using the same peroxide. This congener pattern was found as blank contamination in water samples collected using silicone rubber tubing in the Green River (Greyell and

Williston, 2018). The final non-Aroclor fingerprint was dominated by PCBs 1 (19%), 2 (8%), 3 (19%), 4 (6%), 8 (9%), and 15 (6%). This fingerprint is a reasonably good match for Aroclor 1232 ($R^2 = 0.76$), but since this Aroclor represented only 0.24% of Monsanto's production of Aroclors (Brown, 1994), we deem it unlikely that it arises from Aroclors. Instead, this fingerprint is thought to be associated with silicone and therefore will be called the "phenyl silicone" factor. These congeners and others can be present whenever the silicone is produced from chlorophenylsilanes and these congeners have been found in raw dichlorodiphenylsilane, diphenylsilanediol, and chlorotriphenylsilane (i.e. feedstocks for phenyl silicone production) as well as in finished silicone products such as silicone-based adhesives (Anezaki and Nakano, 2015). The widespread use of silicone-based products, including caulks and adhesives, probably introduced these congeners into the samples, either in the lab or in the field.

The analysis of the blanks themselves indicates that Aroclor formulations remain the main source of PCB blank contamination. The four factors representing Aroclors explain 65% of the PCB mass in the blanks. The peroxide and phenyl silicone factors explain 8% and 9% of the PCBs in the blanks, respectively. The factor associated with PCB 11 explains 18% of the PCB mass in the blanks. The differences in the abundance of these seven factors across the different types of blanks and the different studies were small. Figure S-2 of supporting information demonstrates that although the absolute concentrations of PCBs in the ambient water study blanks are lower than in the other studies, the distribution of the PCBs across the seven factors is similar for all types of blanks. This indicates that efforts to reduce blank contamination seem to have been roughly equally effective for all PCB sources. Of note, the blanks with the highest PCB concentrations (including the outlier blank mentioned above) were more likely to contain higher proportions of blank factors 6 (Aroclor 1254) and 7 (Aroclor 1260). These two factors have the highest average molecular weights. Their abundance in these blanks may indicate contamination from PCB-carrying soil or dust particles.

PMF results from ambient water data sets

Σ_{209}PCB concentrations in the ambient water samples (without blank correction) ranged from 33 pg/L to 2461 pg/L. The mean (171 pg/L) was greater than the median (145 pg/L) and the skewness was 8.1 indicating an approximately log-normal distribution.

Multiple data sets were analyzed using PMF. These are summarized in Table 1. All of these data sets included all 139 samples and varying number of peaks/congeners listed in Table S-1. All data sets resulted in between 5 and 7 resolved factors. Table 1 is organized in order of increasing aggressiveness of the blank correction scheme. This is most notable in the column called "% of PCB mass included." Increasingly aggressive blank correction methods remove greater amounts of mass from the data set. None of the blank correction approaches reported here resulted in all congeners being designated as ND in any sample. All of the permutations of the data set yielded the following five factors: (1) a factor strongly resembling Aroclor 1254 with similarity (R^2) values ranging from 0.80 to 0.98, (2) a factor very similar to Aroclor 1260 with R^2 values ranging from 0.70 to 0.81, (3) a factor similar to Aroclor 1248 with R^2 values ranging from 0.63 to 0.89, (4) one (or sometimes two) factors that were similar to low molecular weight Aroclors 1016 and/or 1242 with R^2 values ranging from 0.35 to 0.84, and (5) a factor dominated by PCB 11. Due to the similarity between the fingerprints of Aroclors 1016 and 1242, we cannot discriminate between the two.

Furthermore, all permutations generally agreed on the contribution of these factors to the total mass of PCBs in the data set (keeping in mind that different data sets contain differing amounts of mass, based on how much mass is discarded during censoring/subtraction). This is presented in Table 1 under the heading "Distribution of PCB mass." Because some of the model solutions identified more than one factor representing Aroclors 1016 and 1242, the contribution of low molecular weight (MW) Aroclors is given and represents the sum of factors representing Aroclors 1016, 1242, and 1248.

When the PMF modeling indicated that the optimal solution contained more than five factors, the additional factors fell into four categories: (1) Aroclors as noted above, (2) the phenyl silicone pattern, (3) the peroxide pattern, and (4) an unidentifiable factor that is generated when aggressive blank subtraction is employed. This unidentifiable factor contained congeners that are present in Aroclors, but in proportions that do not match the Aroclors, such as PCBs 31, 52, 66, and 118. For example, the unidentifiable factor generated by the MaxSub61 data set consisted of 8%, 16%, 13% and 13% of these congeners, respectively. Perdih and Jan (1994) found PCBs 52 and 66 in

silicone, but not PCBs 31 and 118. Anezaki and Nakano (2015) found PCB 31, 52, and 66 in silicone-based products. However, this mystery factor contained almost no contribution from PCBs 44 + 47 + 65 and 45 + 51, suggesting it is not related to peroxide-cured silicone. We speculate that the process of subtracting blank masses introduced a pattern to the data that the PMF program recognized. This pattern may be merely an artifact of the blank subtraction procedure, not an indicator of a unique source of PCBs.

In the interest of brevity, here we discuss only the three most useful model solutions. Additional model results are provided in supporting information.

Uncorrected data set

The data set that received the least blank correction (i.e. none) contained 73 peaks (117 congeners). This low level of blank correction leaves 96.6% of all the PCB mass detected in these sample in the data set submitted for PMF analysis. The 3.4% mass lost is due to the 86 peaks (92 congeners) that were not included in the data set because they were rarely detected. The fingerprints of the factors generated by this data set are very similar to those generated from the blank data, i.e. seven factors were generated with four representing Aroclors and the other three representing PCB 11, peroxide and phenyl silicone (Figure 2). When compared to the results from the blank-corrected data sets (see below), this result indicates that if blank correction is not performed, the resulting PMF results will be erroneous, i.e. they will identify sources of PCBs that do not truly impact the water column. Blank correction is therefore essential to producing meaningful fingerprinting results when the concentrations in the samples are similar to those in the blanks. Specifically, the results suggest that silicone products are sources of PCBs to blanks but not to samples, i.e. it is probably not the use of silicone products in the sampling media or field equipment that contributes PCBs to the samples, but rather the silicone products used in the lab, since PCBs from silicone are found at similar levels in both method and travel blanks as well as uncorrected samples.

Censored data set

The censored data set containing the most congeners and employing the least aggressive blank correction method was BatchCensor68. Full results of this data set are given in supporting information Tables S-2 and S-3. Censoring at one times the batch-specific blank concentrations leaves 90.7% of the mass originally detected in these samples to be submitted for PMF analysis, i.e. only 5.9% of the PCB mass was lost during censoring compared the Uncor73 data set. This data set generated only the five basic factors, shown in Figure 3. Note that the resemblance between the factors generated and the Aroclors was quite strong. Although this data set did contain PCBs 44 + 47 + 65 and 45 + 51, the peroxide factor was not generated. Concentrations of these two peaks are well described, with R^2 values for the measured versus the model-predicted concentrations of 0.80 and 0.67, respectively. Most of their mass was contained in the factor that resembled Aroclor 1248. PCBs 1 and 3 were not included in this data set because the censoring routine caused a majority of their measurements to be designated as ND, and therefore the phenyl silicone factor was not generated. This result demonstrates that two of the factors produced via PMF analysis of the uncorrected data set do not represent sources of PCBs to the water column, but rather represent blank contamination. Blank correction is therefore essential when the concentrations of the analytes in the samples are similar to those in the blanks.

A complete discussion of the G matrix results is beyond the scope of this investigation, but the G matrix can indicate whether blank contamination is important even after blank correction schemes have been applied. For example, if blank contamination continued to impact the data set, we might expect that PCB sources would vary randomly in time and space, or that some sources might show little variability regardless of location or timing of sampling. The G matrix instead shows some expected trends. At some sampling locations (SR3 and SR4), PCB concentrations decrease as river flow increases ($p < 0.05$), i.e. there is a dilution effect as is often seen in rivers (Meharg et al., 2003; Fu and Wu, 2006). This dilution is driven by decreases in BathCensor68F2 (Aroclors 1016/1242) and BathCensor68F3 (Aroclor 1248) at both sites, with BathCensor68F1 (PCB 11) also displaying significant ($p < 0.05$) dilution at SR3. This makes sense since these lower molecular weight fingerprints are those most likely to be in the dissolved phase. In contrast, higher molecular weight factors are more likely to reside in the particle phase, and high river flow could induce scour leading to higher particle loads in the water column, negating any dilution effect. In terms of spatial trends, Figure 4 shows a typical low-flow sampling event. PCB concentrations are low at SR15, which is located at the Post Falls dam at the outlet of Lake Coeur d'Alene.

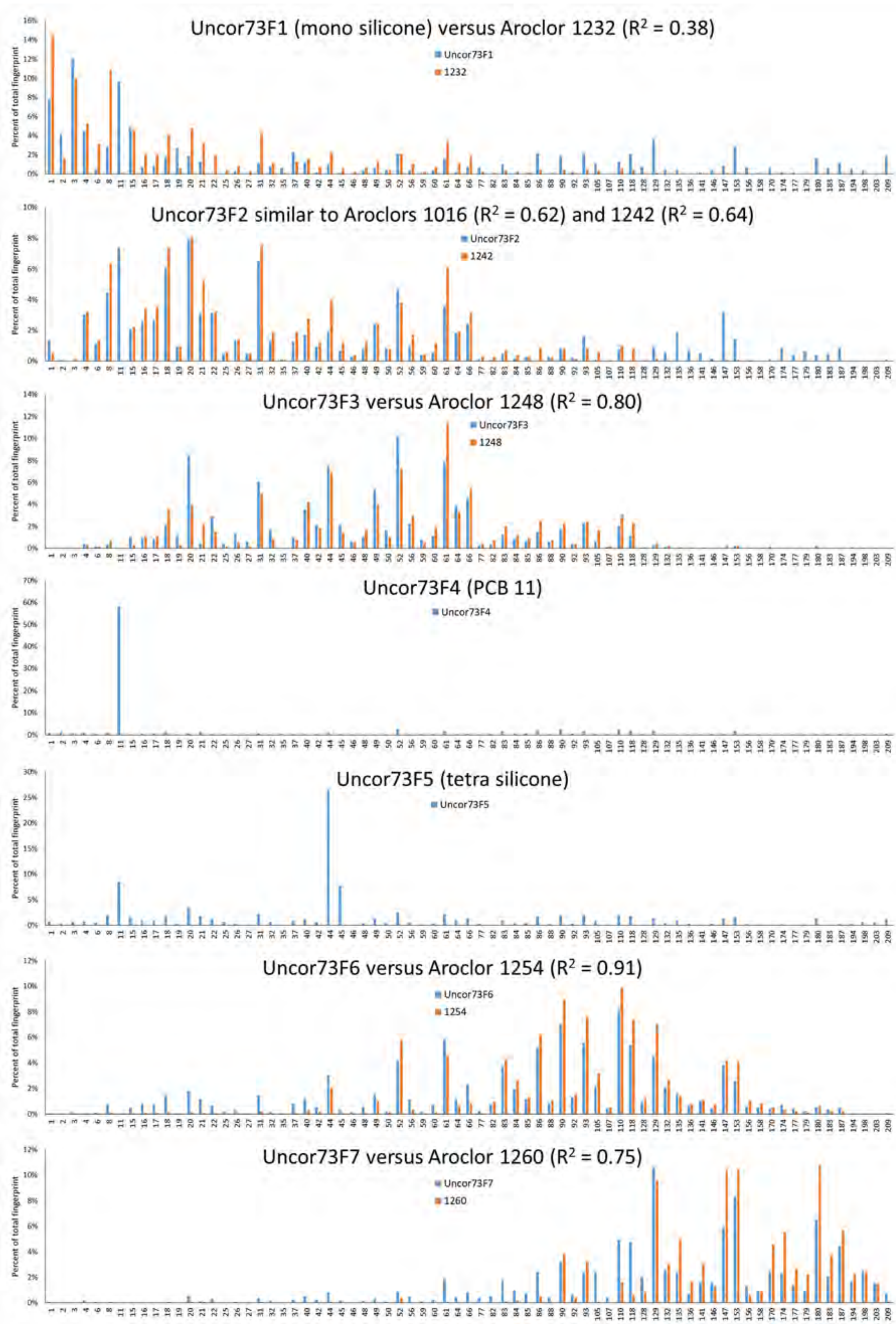

Figure 2. The seven factors isolated by PMF analysis for the Uncor73 data set, compared with their best-match Aroclors. PCBs are identified by their IUPAC numbers on the x axis, with only the lowest IUPAC number listed for coelutions. A full list of coeluting congeners is provided in supporting information Table S-1. Uncor73F1 is thought to be related to phenylsilanes, but is compared with Aroclor 1232 here.

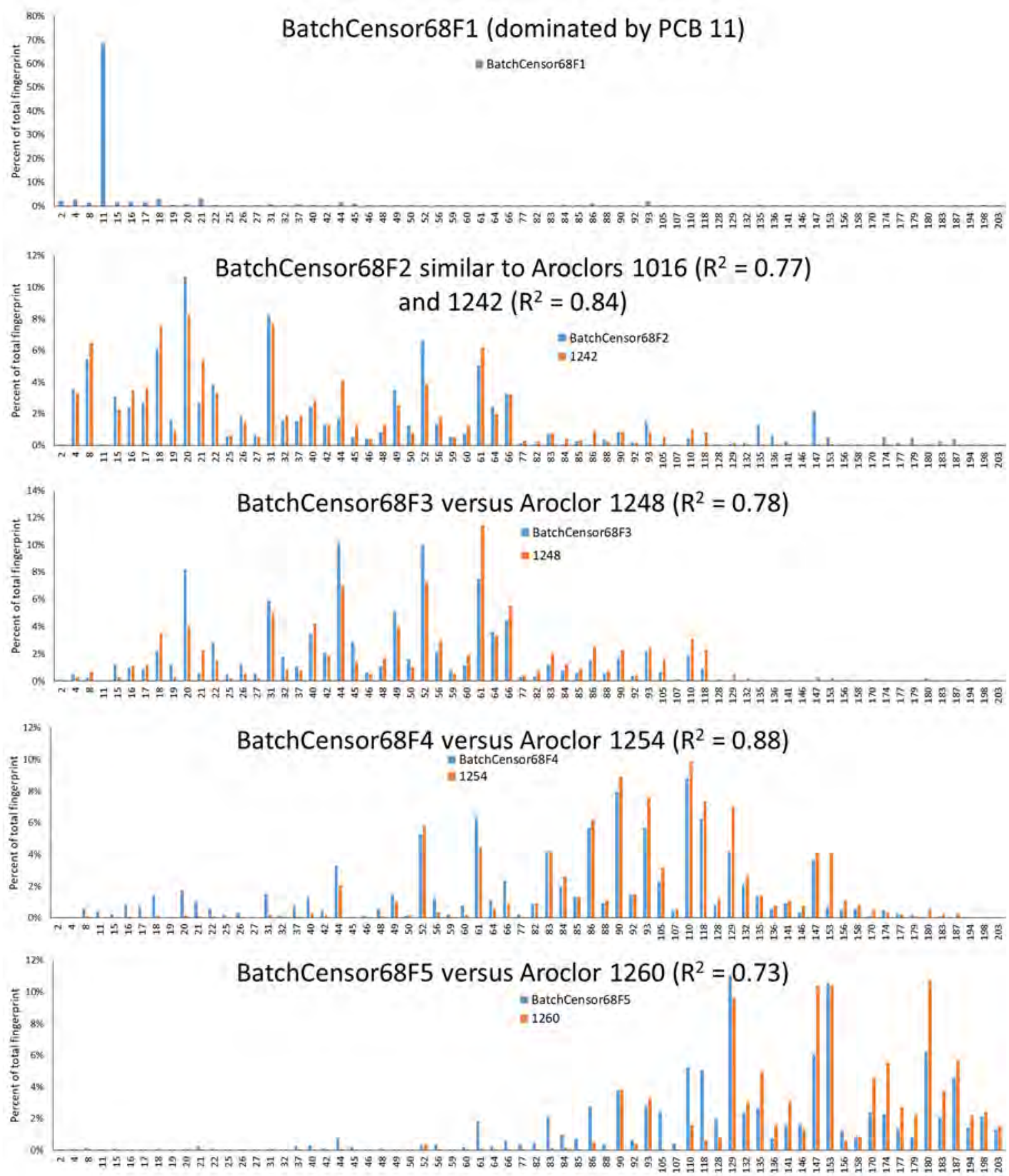

Figure 3. PMF generated factors for the BatchCensor68 data set showing the five basic factors produced by all permutations of the data set. PCBs are identified by their IUPAC numbers on the x axis, with only the lowest IUPAC number listed for coelutions. A full list of coeluting congeners is provided in supporting information Table S-1.

Concentrations increase as the river flows through the populated areas around Spokane. The concentration of BathCensor68F3 (Aroclor 1248) increases as the river flows from SR8 to SR7 ($p < 0.05$ via paired two-tailed t test) by an average of 91 pg/L Σ_{112}PCBs. Only four low-flow (about 700 cfs) events sampled both of these sites. Twelve events sampled at both SR9 and SR7. During these twelve events, the concentration of BathCensor68F3 (Aroclor 1248) again increased ($p < 0.05$) by an average of 125 pg/L Σ_{112}PCBs as the river flowed from SR9 to SR7. This represents a significant loading in a river where the average Σ_{112}PCBs is 157 pg/L. This loading was expected since there is a known source of Aroclor 1248 between these two sampling sites (LimnoTech, 2016).

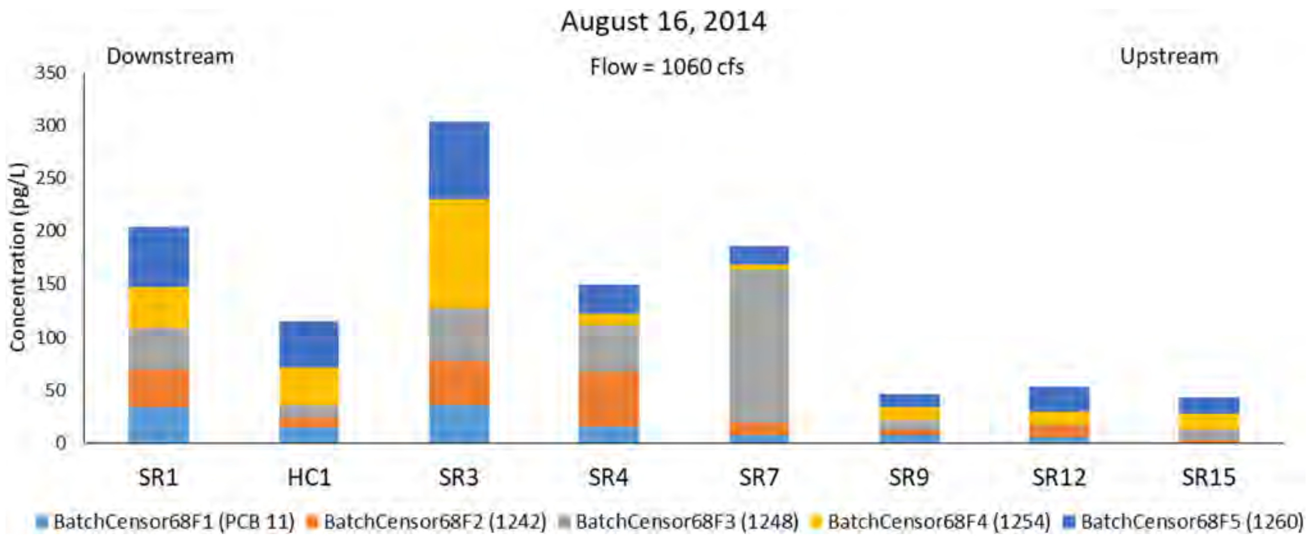

Figure 4. Spatial variation in results based on the BatchCensor68 PMF solution from a typical low-flow sampling event. Minimum flow in the Spokane River is about 700 cfs. The maximum flow sampled was 15,400 cfs. Site abbreviations are given the caption to Figure 1.

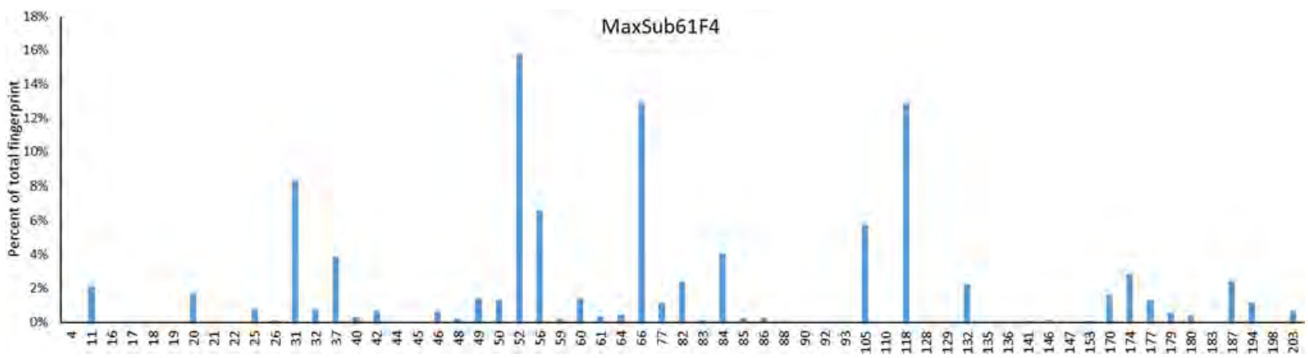

Figure 5. The unidentifiable factor produced when aggressive blank subtraction is used (from data set MaxSub61). PCBs are identified by their IUPAC numbers on the x axis, with only the lowest IUPAC number listed for coelutions. A full list of coeluting congeners is provided in supporting information Table S-1.

Subtracted data set

Among the most aggressive blank correction methods investigated involved subtracting the maximum concentration detected across all blanks from the sample (MaxSub61). This resulted in just 51.4% of the total PCB mass originally detected in the samples being included in the data set submitted for PMF analysis. Determining the optimal number of factors for this data set was difficult (see supporting information for the criteria used to determine the optimal number of factors). Nine of ten seed runs were in agreement for the six factor solution. The five factor solution was bifurcated with four of the seed runs agreeing with each other and the other six similar to each other. All ten seed runs of the four factor solution were in agreement, but this solution was judged inferior because all of the other permutations had produced the five basic factors, and this solution generated one factor representing a mix of Aroclors 1016/1242 and 1248. The extra unidentifiable factor generated from the six factor solution is shown in Figure 5. Note that it contains almost no 44 + 47 + 65 and 45 + 51. It is not similar to any of the Aroclors.

Conclusions

The purpose of this study was to identify which approach (or combination of approaches) best addresses the impact of blank contamination on the analysis of low levels of PCB measured in the Spokane River water column. PMF was successfully applied to these data sets and told a consistent story about PCB contamination in the Spokane River. All of the various PMF models suggested that Aroclors are the dominant source of PCBs to the Spokane River. All suggest that PCB 11 is present in the river at levels

that cannot be accounted for by blank contamination, and that sources of PCB 11, probably pigments, are responsible for a small fraction of the PCB problem in the Spokane River. It is important to note that while the factor containing most of the PCB 11 mass accounts for 8% to 15% of total PCB mass in these data sets, this does not imply that 8% to 15% of PCBs in the Spokane River come from non-Aroclor sources. In other systems, PCB 11 has been associated with secondary sources such as stormwater. For example, in the Delaware River, the factor containing most of the PCB 11 mass was thought to be associated with stormwater and combined sewer overflows because it was more prevalent at high river flow (Du et al., 2008). If the same is true in the Spokane River, the other PCBs in this factor may arise from Aroclors, but have undergone a great deal of weathering. These congeners may be moving with PCB 11 via the same transport mechanism even though they have a different primary source.

Selection of best approach(es)

The criteria used to evaluate the success of each approach were as follows:

1. The approach should generate a stable PMF model solution.
2. The model solution should be interpretable, i.e. the results make sense based on everything we know about PCB contamination in general and in the Spokane River in particular. In this respect, we have an advantage in analyzing PCB data, because the source terms are well-defined. It is known that Aroclors are the primary PCB sources almost everywhere in the United States, and the congener patterns of the Aroclors are remarkably constant since only one company, Monsanto, was responsible for about 99% of all U.S. production of PCBs (ATSDR, 2000).
3. Other criteria being met, the bias should be toward using the approach that includes the largest amount of mass and the largest number of peaks possible.

Based on the first criterion, all data sets converged on a solution. The selection of the optimal number of factors was difficult for the MaxSub61 data set, due to some instability in the model solution as described above.

In order to evaluate the approaches under criterion two, we need to determine whether the factors produced by the PMF analysis are "real," i.e. they reflect the actual conditions in the river, or are "artificial," i.e. they are due to blank contamination. The fact that the same five basic factors are produced by all model runs suggests that these five factors at least are "real." Note that this implies that PCB 11 contamination in the Spokane River is real. There is no method of blank correction that makes the PCB 11-dominated factor disappear. The approaches using blank subtraction generated an uninterpretable factor that did not appear in any other model runs. Therefore, this factor does not represent a "real" source of PCBs to the river, and this approach of blank subtraction fails under criterion #2. The preponderance of evidence suggests that the phenyl silicone factor is an artifact, since it does not appear in any model run except those for which no blank correction of any kind is performed. The peroxide factor is a bit more robust, but this is likely due to the fact that PCBs 44 + 47 + 65 and 45 + 51 are present in the Aroclors, such that these congeners are real contaminants in the river, and blank correction does not, and should not, eliminate them. The peroxide factor was not produced by the vast majority of data sets that included 68 or 61 congeners (i.e. that included these two peaks). Therefore, we conclude that the tetra silicone factor results from blank contamination, suggesting that model runs that do not generate this factor are acceptable. Since all of the runs utilizing blank censoring produced the same basic five factors, they are all acceptable under criterion #2.

Criterion #3 calls for the model to incorporate as much of the data as possible. This criterion suggests that we should utilize the batch-specific blank concentration(s) instead of the maximum concentration across all blanks. Further, this criterion suggests that we should use the longest congener list possible. In this study, BatchCensor68 satisfies criterion #3 the best. Retaining PCBs 44 + 47 + 65 and 45 + 51 allows us to use the PMF model to determine whether contamination from peroxide-cured polymers (probably silicones) is significant. Eliminating these congeners may leave us blind to this source of contamination and is not recommended for PCB data sets.

Based on these results, the following procedures are recommended for all data sets, not just those involving PCBs:

1. Blanks and samples should both be carefully examined for patterns prior to PMF analysis.
2. Conducting PMF analysis on the concentrations in the blanks proved to be very useful in

identifying the sources of PCBs to blanks. We recommend that this be performed for all types of data sets when sufficient data is available.
3. Blank censoring should be performed on the data at one times the batch-specific blank concentration.
4. Analytes should not be discarded solely because they may be associated with blanks, because this may leave the operator blind to some sources of contamination.
5. PMF analysis of the uncorrected data set was useful. We recommend conducting such an analysis using the same analyte list as in recommendation 3 above so that the results may be compared.

Acknowledgements

We thank the Spokane River Regional Toxics Task Force for funding this study and providing the data. Richard Grace (SGS AXYS) provided helpful comments. LAR provides expert testimony on behalf of the city of Spokane, WA and other plaintiffs in a series of lawsuits against Monsanto.

ORCID

Lisa A. Rodenburg http://orcid.org/0000-0002-6828-173X

References

Agency for Toxic Substances and Disease Registry (ATSDR). 2000. *Toxicological Profile for Polychlorinated Biphenyls (PCBs)*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Anezaki, K., and Nakano, T. 2015. Unintentional PCB in chlorophenylsilanes as a source of contamination in environmental samples. *Journal of Hazardous Materials* 287:111–117. doi: 10.1016/j.jhazmat.2015.01.026

Brown, J. F. 1994. Determination of PCB metabolic, excretion, and accumulation rates for use as indicators of biological response and relative risk. *Environmental Science & Technology* 28:2295–2305. doi: 10.1021/es00062a013

Contamination Assessment and Reduction Project (CARP). 2007. *Data Archive: Water, Sediment and Biota Data Collected from 1999-2003. CD-ROM*. New York, NY: Hudson River Foundation.

Department of Ecology, State of Washington. 2018. *Water Quality Program Permit Writer's Manual*. Washington State Department of Ecology Water Quality Program: Olympia, WA. 555 pp.

Du, S., Belton, T. J., and Rodenburg, L. A. 2008. Source apportionment of polychlorinated biphenyls in the tidal Delaware River. *Environmental Science & Technology* 42: 4044–4051. doi: 10.1021/es703047a

Ferrario, J., Byrne, C., and Dupuy, A. E. 1997. Background contamination by coplanar polychlorinated biphenyls (PCBs) in trace level high resolution gas chromatography high resolution mass spectrometry (HRGC/HRMS) analytical procedures. *Chemosphere* 34(11):2451–2465. doi: 10.1016/S0045-6535(97)00083-0

Fu, C. T., and Wu, S. C. 2006. Seasonal variation of the distribution of PCBs in sediments and biota in a PCB-contaminated estuary. *Chemosphere* 62(11):1786–1794. doi: 10.1016/j.chemosphere.2005.07.034

Greyell, C., and Williston, D. 2018. *Green River PCB Equipment Blank Study Data Report*. Seattle, WA: King County Water and Land Resources Division.

Herkert, N. J., Jahnke, J. C., and Hornbuckle, K. C. 2018. Emissions of tetrachlorobiphenyls (PCBs 47, 51, and 68) from polymer resin on kitchen cabinets as a non-aroclor source to residential air. *Environmental Science & Technology* 52(9):5154–5160. doi: 10.1021/acs.est.8b00966

Hetling, L., Horn, E., and Tofflemire, J. 1978. *Summary of Hudson River PCB Study Results*. Albany, NY: New York State Department of Environmental Conservation.

Hsieh, P. A., Barber, M. E., Contor, B. A., Md. Hossain, A., Johnson, G. S., Jones, J. L., et al. 2007. Ground-water flow model for the Spokane Valley-Rathdrum Prairie Aquifer, Spokane County, Washington, and Bonner and Kootenai Counties, Idaho, USGS Scientific Investigations Report 2007–5044. 78 pp.

Kim, E., Hopke, P. K., and Qin, Y. J. 2005. Estimation of organic carbon blank values and error structures of the speciation trends network data for source apportionment. *Journal of the Air & Waste Management Association* 55(8):1190–1199. doi: 10.1080/10473289.2005.10464705

LimnoTech. 2014a. Quality assurance project plan: Spokane River toxics reduction strategy study. Prepared for the Spokane River Regional Toxics Task Force. Limnotech, Available at: http://srrttf.org/wp-content/uploads/2014/03/QAPP_Draft_03-24-14.pdf (accessed September 12, 2019).

LimnoTech. 2014b. Sampling and analysis plan: Spokane River toxics reduction strategy study. Prepared for the Spokane River Regional Toxics Task Force. Limnotech, Available at: http://srrttf.org/wp-content/uploads/2014/02/Spokane_SAP-Feb12_14_.pdf (accessed September 12, 2019).

LimnoTech. 2015. Spokane River regional toxics task force phase 2 Technical activities report: Identification of potential unmonitored dry weather sources of PCBs to the Spokane River. Prepared for the Spokane River Regional Toxics Task Force.

LimnoTech. 2016. *2016 Comprehensive Plan to Reduce Polychlorinated Biphenyls (PCBs) in the Spokane River*. Ann Arbor, MI: Spokane River Regional Toxics Task Force.

Litten, S., Fowler, B. I., and Luszniak, D. 2002. Identification of a novel PCB source through analysis of 209 PCB congeners by US EPA modified method 1668. *Chemosphere* 46:1457–1459. doi: 10.1016/S0045-6535(01)00253-3

Meharg, A. A., Wright, J., Leeks, G. J. L., Wass, P. D., Owens, P. N., Walling, D. E., et al. 2003. PCB congener dynamics in a heavily industrialized river catchment. *The Science of the Total Environment* 314:439–450. doi: 10.1016/S0048-9697(03)00067-6

Norris, G., Duvall, R., Brown, S., and Bai, S. 2014. *EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide. EPA/600/R-14/108*. Washington, DC:

U.S. Environmental Protection Agency Office of Research and Development.

Norris, G., Katie Wade, K., Zahn, P., Brown, S., Paatero, P., Eberly, S., et al. 2009. *Guidance Document for PMF Applications with the Multilinear Engine*. Research Triangle Park, NC: U.S. EPA.

Paatero, P. 2000. *User's Guide for Positive Matrix Factorization Programs PMF2 and PMF3. Part 1: Tutorial*, US Environmental Protection Agency.

Paatero, P., and Tapper, U. 1994. Positive matrix factorization - A nonnegative factor model with optimal utilization of error-estimates of data values. *Environmetrics* 5: 111–126. doi: 10.1002/env.3170050203

Perdih, A., and Jan, J. 1994. Formation of polychlorobiphenyls in silicone-rubber. *Chemosphere* 28(12): 2197–2202. doi: 10.1016/0045-6535(94)90187-2

Polissar, V. A., and Hopke, P. H. 2001. Atmospheric aerosol over Vermont: Chemical composition and sources. *Environmental Science & Technology* 35:4604–4621. doi: 10.1021/es0105865

Praipipat, P., Rodenburg, L. A., and Cavallo, G. J. 2013. Source apportionment of polychlorinated biphenyls in the sediments of the Delaware River. *Environmental Science & Technology* 47:4277–4283. doi: 10.1021/es400375e

Rodenburg, L. A., Du, S., Xiao, B., and Fennell, D. E. 2011. Source apportionment of polychlorinated biphenyls in the New York/New Jersey Harbor. *Chemosphere* 83: 792–798. doi: 10.1016/j.chemosphere.2011.02.058

Rodenburg, L. A., and Delistraty, D. A. 2019. Alterations in fingerprints of polychlorinated biphenyls in benthic biota at the Portland Harbor Superfund Site (Oregon, USA) suggest metabolism. *Chemosphere* 223:74–82. doi: 10.1016/j.chemosphere.2019.02.039

Rodenburg, L. A., Delistraty, D. A., and Meng, Q. 2015a. Polychlorinated biphenyl congener patterns in fish near the Hanford Site (Washington State, USA). *Environmental Science & Technology* 49(5):2767–2775. doi: 10.1021/es504961a

Rodenburg, L. A., Krumins, V., and Curran, J. C. 2015b. Microbial dechlorination of polychlorinated biphenyls, dibenzo-p-dioxins, and -furans at the Portland Harbor Superfund Site, Oregon, USA. *Environmental Science & Technology* 49(12):7227–7235. doi: 10.1021/acs.est.5b01092

Rodenburg, L. A. and Leidos, 2017. *Green-Duwamish River Watershed PCB Congener Study: Phase 2 Source Evaluation*. Seattle, WA.

Rodenburg, L. A., and Meng, Q. 2013. Source apportionment of polychlorinated biphenyls in Chicago Air from 1996 to 2007. *Environmental Science & Technology* 47(8): 3774–3780. doi: 10.1021/es305024p

Rushneck, D. R., Beliveau, A., Fowler, B., Hamilton, C., Hoover, D., Kaye, K., et al. 2004. Concentrations of dioxin-like PCB congeners in unweathered Aroclors by HRGC/HRMS using EPA Method 1668A. *Chemosphere* 54:79–87. doi: 10.1016/S0045-6535(03)00664-7

Spokane County Water Reclamantion. 2015. *Spokane County Regional Water Reclamation Facility NPDES Permit WA-0093317 Revision 3 Quality Assurance Project Plan*. Spokane, WA. 146 pp.

The Japanese Ministry of Economy Trade and Industry (METI). 2012. Summarized results of the second investigation into the presence of polychlorinated biphenyls (PCBs) as by-products in organic pigments. Available at: www.meti.go.jp/english/2012/0528_02.html (last accessed November 15, 2014).

The Japanese Ministry of Economy Trade and Industry (METI). 2014. Compiled results or reanalysis of the presence of polychlorinated biphenyls (PCBs) as by-products in organic pigments. Available at: www.meti.go.jp/english/press/2013/0510_02.html (accessed November 15, 2014).

United Nations Environment Program. 2001. *Final Act of the Conference of Plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants*. Geneva, Switzerland: United Nations Environment Program. 44 pp.

US EPA. 1992. *Hazard Ranking System Guidance Manual*. Washington, DC: United States Environmental Protection Agency Office of Solid Waste and Emergency Response. 30 pp.

US EPA. 1999. *Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS*. Washington DC: United States Environmental Protection Agency.

US EPA. 2014. Method 8270E (SW-846): Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Washington, DC.

Zhao, W. X., Hopke, P. K., Norris, G., Williams, R., and Paatero, P. 2006. Source apportionment and analysis on ambient and personal exposure samples with a combined receptor model and an adaptive blank estimation strategy. *Atmospheric Environment* 40(20):3788–3801. doi: 10.1016/j.atmosenv.2006.02.027

Sources of Polychlorinated Biphenyl Blank Contamination and Their Impact on Fingerprinting

SUPPORTING INFORMATION

Three tables

Two figures

Quality assurance of ambient water PCB measurements

Sampling and analysis was completed in compliance with the sampling and analysis plan (LimnoTech 2014b) and the quality assurance project plan (LimnoTech 2014a). Water samples for PCB analysis were collected in amber glass bottles and shipped to SGS AXYS (British Columbia, Canad) for analysis via method 1668C (U. S. EPA 2010).

In compliance with method 1668C, 31 ^{13}C-labelled surrogate compounds were used, and all data (blanks and samples) were corrected for surrogate recoveries. Method 1668C stipulates that labeled surrogate recovery in samples must be between 5% and 145% for lower molecular weight PCB surrogates (labelled PCBs 1, 3, 4, 15, 19, 28, 37, and 54) and between 10% and 145% for all other surrogates (labelled PCBs 77, 81, 104, 105, 111, 118, 123, 126, 155, 156+157, 167, 169, 170, 178, 180, 188, 189, 202, 205, 206, 208, and 209) (U. S. EPA 2010). In the ambient water data set, average surrogate recoveries ranged from 44% (^{13}C-PCB 1) to 87% (^{13}C-PCB 105). The standard deviations of the surrogate recoveries were used to construct the uncertainty matrix for PMF analysis. These ranged from 9.1% to 17.0%. In this work, the Method Detection Limits (MDLs) were used in the PMF input. MDLs represent the “minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero” (U. S. EPA 2010). The MDLs were calculated by the contract lab and provided for all data points. MDLs ranged from 0.181 pg/L to 6.09 pg/L. The average MDL was 0.313 pg/L and the median was 0.212 pg/L.

Types of blanks

For the other study (Spokane County Water Reclamantion 2015), three types of blanks were collected. **Rinsate** blanks were created by pumping ultrapure water provided by the contract lab through the sampling device after it was cleaned but before it was used for sampling. **Travel** blanks consist of unopened/sealed bottles of ultrapure water provided by the contract lab that traveled with the samples. **Method** blanks were an “analyte free matrix”, i.e. HPLC grade water, prepared and analyzed by the contract laboratory.

PMF analysis

PMF2 was operated in "robust" mode so that outlier values would not skew the factor profiles (Reff, Eberly, and Bhave 2007; Norris et al. 2009). The model was run for multiple cases, including varying assumptions of 3 to 8 factors, and the model was run 10 times at 10 different starting points (i.e., seed values) for each case. The output was used to identify which number of factors provides the optimal model solution.

Selection of the optimal number of factors

All forms of factor analysis require the operator to identify the optimal number of factors, or source fingerprints, that adequately describe the data set (Reff, Eberly, and Bhave 2007). The current analysis used four main criteria to determine the 'best' number of factors. These criteria are similar to those proposed by Reff, Eberly, and Bhave (2007), except that the comparison of the theoretical and calculated 'Q' values was not relied upon to indicate the correct number of factors. This approach was rejected because the calculated 'Q' depends on the uncertainty matrix (Equation 2). When uncertainties are inaccurate, the theoretical and calculated 'Q' values can differ substantially (Polissar and Hopke 2001).

The first and most important criterion is that the factors must be interpretable and useful for source apportionment of contaminants. For PCBs, this means that most of the resolved factors should at least somewhat resemble the original Aroclor formulations produced by Monsanto, because these are the source of the vast majority of all PCBs produced in the United States.

Second, the model solution should be stable. This is determined by running the model from many different starting points (i.e., seed values) for a given number of factors and determining whether all or most of them converge on the same solution. Similar solutions will have essentially the same 'Q' value, 'G' matrix, and 'F' matrix. The relative standard deviation of 10 seed runs of the 'G' matrix is used as an indicator of model stability (RSD-G). As noted above, there are many ways to adjust the input matrix to attain a stable solution. The 'Q' value is a function of the similarity between the measured and modeled concentrations. All else equal, a lower 'Q' value indicates a better model fit. Thus, the seed run with the lowest 'Q' value is used for all interpretations of the model results.

Third, the model solution should adequately describe the data (i.e., there should be reasonably close agreement between the measured and modeled concentrations). This is primarily evaluated by calculating the unadjusted R^2 value between the measured and modeled concentrations by analyte (i.e., PCB peak). In theory, requesting more factors should allow the model to produce a better fit to the measured data. Deterioration of the model fit when additional factors are requested is usually a sign of over-fitting (i.e., too many factors have been requested).

Fourth, a multiple linear regression of the 'G' matrix versus the measured sum of analytes should yield positive and statistically significant coefficients for all factors.

Treatment of non-detects

In the context of forensic (i.e. legal) work, we need to consider whether the treatment of non-detects is *scientifically* defensible and whether it is *legally* defensible. In this work, non-detects have been assigned a proxy value that consists of a random number between zero and the detection limit, in accordance with much of our previous work using PMF2 (Rodenburg and Meng 2013; Rodenburg et al. 2010). Our research group generally uses this approach when non-detects comprise more than about 10% of the data points. When less than 10% of the data points are non-detects, we typically use half the detection limit (Rodenburg and Delistraty 2019; Rodenburg and Ralston 2017), since this approach is simpler and at low proportions of non-detects, using half the limit of detection versus a random proxy value seems to make no difference to the PMF solution. The fact that we have published peer-reviewed papers using both of these approaches to the treatment of non-detects sets a precedent that renders these approaches legally defensible. In addition, since the random numbers between 0 and the LOD average out to LOD/2, both approaches satisfy the EPA's guidance on this issue, which states that (Regional Guidance on Handling Chemical Concentration Data Near the Detection Limit in Risk Assessments, EPA 2017):

- "B. Non-detection v. zero concentration. Risk assessors have the following methods to choose from, for handling data below the DL:
    - 1. Non-Detects handled as DLs - In this highly conservative approach, all non-detects are assigned the value of the DL, the largest concentration of analyte that could be present but not detected. This method always produces a mean concentration which is biased high, and is not consistent with Region III's policy of using best science in risk assessments.
    - 2. Non-Detects reported as zero - This is the best-case approach, in which all undetected chemicals are assumed absent. This method should be used only for specific chemicals which the risk assessor has determined are not likely to be present…
    - 3. Non-Detects reported as half the DL - This approach assumes that on the average all values between the DL and zero could be present, and that the average value of non-detects could be as high as half the detection limit. This method (or method 4, below) should be used for chemicals which the risk assessor has determined may be present below the DL…
    - 4. Statistical estimates of concentrations below the DL - Use of statistical methods to estimate concentrations below the DL is technically superior to method 3 above, but also requires considerably more effort and expertise than the three simpler methods. Also, these statistical methods are effective only for data sets having a high proportion of detects (typically, greater than 50%). Therefore, statistical predictions of concentrations below the DL…are recommended only for compounds which significantly impact the risk assessment and for which data are adequate."

Note that this passage refers to treatment of non-detects in risk assessment. We are not aware of any guidelines from EPA on the treatment of non-detects for fingerprinting, so we have

followed these guidelines. Basically they say that when we can reasonably assume that PCBs are present, then we should treat non-detects as half the detection limit. This is a legally defensible position.

Note that option 4, which might involve the use of more sophisticated approaches, is probably more *scientifically* defensible than using LOD/2, but is also more complicated and open to interpretation, meaning that it might lead us into a complicated *legal* quagmire. The more sophisticated methods (Huang et al. 2019; Haslauer et al. 2017; Antweiler 2015) for estimating values below the detection limit (i.e. 'left-censored' data) would result in the average proxy values being greater than LOD/2 and to our knowledge have not been used previously to construct PMF inputs in peer-reviewed publications. The average proxy value would be greater than LOD/2 because we have included congeners/peaks in the PMF input only when they are detected in more than half of the samples, i.e. we have selected data for which the LOD is less (and often much less) than the median. In such cases, the shape of the distribution function for the data less than the LOD is such that higher values closer to the LOD are much more probable than lower values closer to zero. As a result, the average is significantly higher than LOD/2. This is true regardless of whether the data is normally or log-normally distributed.

Nevertheless, we explored the possibility of using some of these more sophisticated techniques to estimate proxy values for non-detects. In doing so, we ran into two problems. The first, relatively minor, problem is that the reported LODs are different for every sample and every PCB congener. In addition, the LOD values are sometimes similar to the measured concentrations. For example, for PCB 4, 41 of the 139 data points were not detected (even before any blank correction). Detected concentrations ranged from 0.36 pg/L to 4.75 pg/L and LODs ranged from 0.183 pg/L to 6.09 pg/L. It is therefore difficult to characterize and quantify the distribution of the data when some of the detections are less than some of the LODs.

The second and more difficult issue is that the present work considers two kinds of non-detects: (1) true non-detects, in which the congener was not detected in the sample during instrumental analysis, and (2) designated non-detects, in which the congener was detected by the instrument, but at concentration less than the blank, such that we designated the data point as a non-detect. To complicate matters further, the concentrations of PCBs in the various blanks used for correction (either censoring and subtraction) are different for each congener and sampling event. Many publications (some of which are cited above) outline ways to handle true non-detects, but we are not aware of any publications that handle the second type of designated or blank corrected non-detect. As a result, we determined that using more sophisticated approaches to estimating the values of non-detects was beyond the scope of the present work.

Table S-1. Peaks and coeluting congeners included in each permutation of the surface water (left) and blank (right) data sets analyzed by PMF. Coelutions are (roughly) listed in order from the most abundant congener in the peak to the least.

59 peaks		61 peaks		68 peaks		73 peaks			42 peaks (blank data set)	
Lowest IUPAC	coelutions	Lowest IUPAC	coelutions	Lowest IUPAC	coelutions	Lowest IUPAC	coelutions		Lowest IUPAC	coelutions
		all congeners to the left		all congeners to the left		all congeners to the left				
4		plus		plus		plus			1	
11		44	44/47/65	2		1			2	
16		45	45/51	8		3			3	
17				15		6			4	
18	30/18			27		35			8	
19				107	107/124	209			11	
20	28/20			156	156/157				15	
21	21/33			158					16	
22									17	
25									18	30/18
26	26/29								20	28/20
31									21	21/33
32									22	
37									26	26/29
40	41/40/71								31	
42									32	
46									37	
48									40	41/40/71
49	69/49								44	44/47/65
50	50/53								45	45/51
52									49	69/49
56									52	
59	59/62/75								56	
60									60	
61	61/70/74/76								61	61/70/74/76
64									64	
66									66	
77									68	
82									83	
83									86	108/119/86/97/125/87
84									90	113/90/101
85	117/116/85								93	95/100/93/102/98
86	108/119/86/97/125/87								105	
88	88/91								110	110/115
90	113/90/101								118	
92									129	138/163/129/160
93	95/100/93/102/98								135	151/135/154
105									147	147/149
110	110/115								153	153/168
118									180	180/193
128	128/166								187	
129	138/163/129/160								209	
132										
135	151/135/154									
136										
141										
146										
147	147/149									
153	153/168									
170										
174										
177										
179										
180	180/193									
183	183/185									
187										
194										
198	198/199									
203										

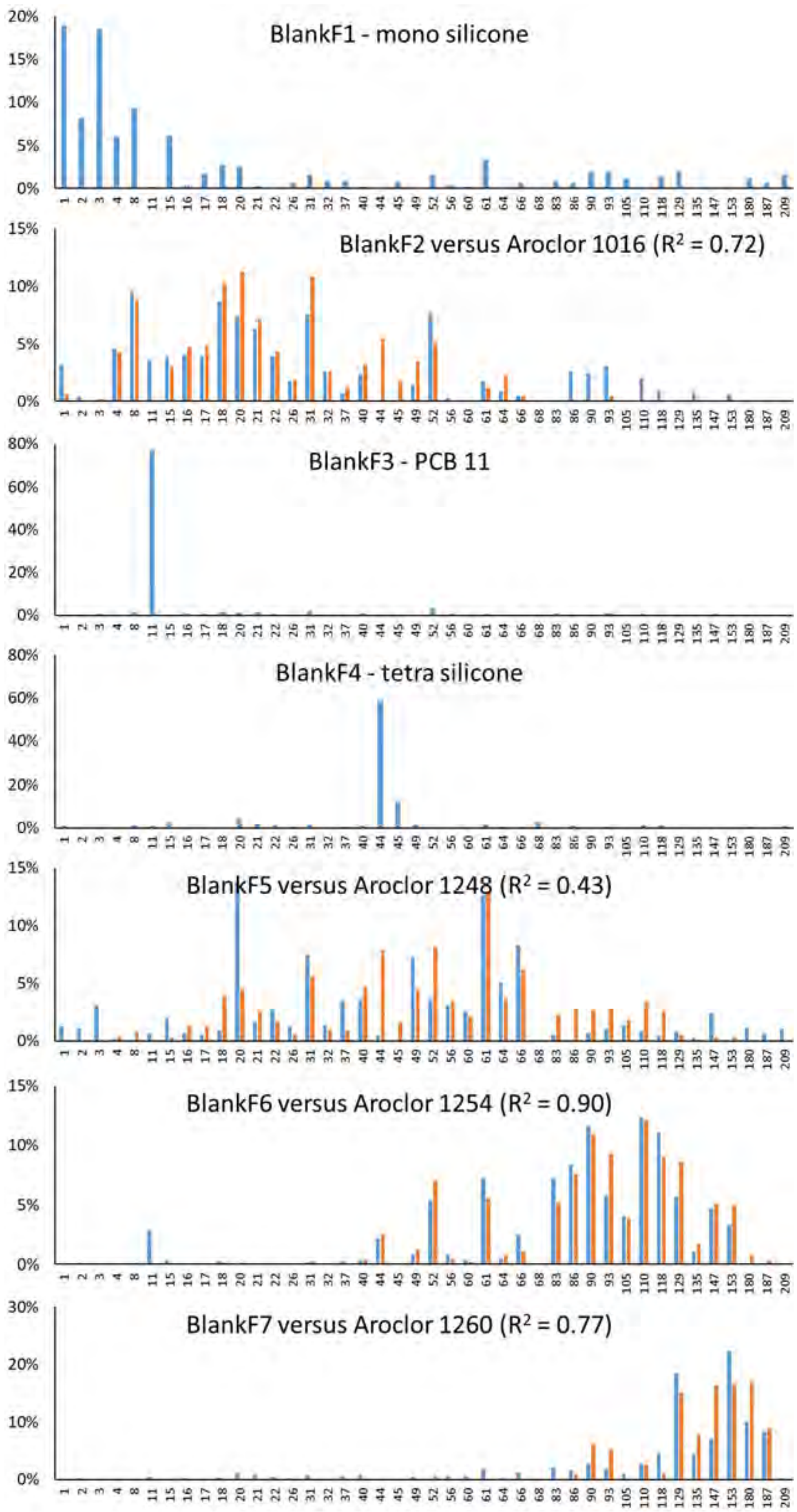

Figure S-1. Fingerprints generated from the blank data set (42 peaks). The x-axis is labelled with the IUPAC numbers of the congeners. For coelutions, only the lowest IUPAC number is shown. Coelutions are listed in table S-1.

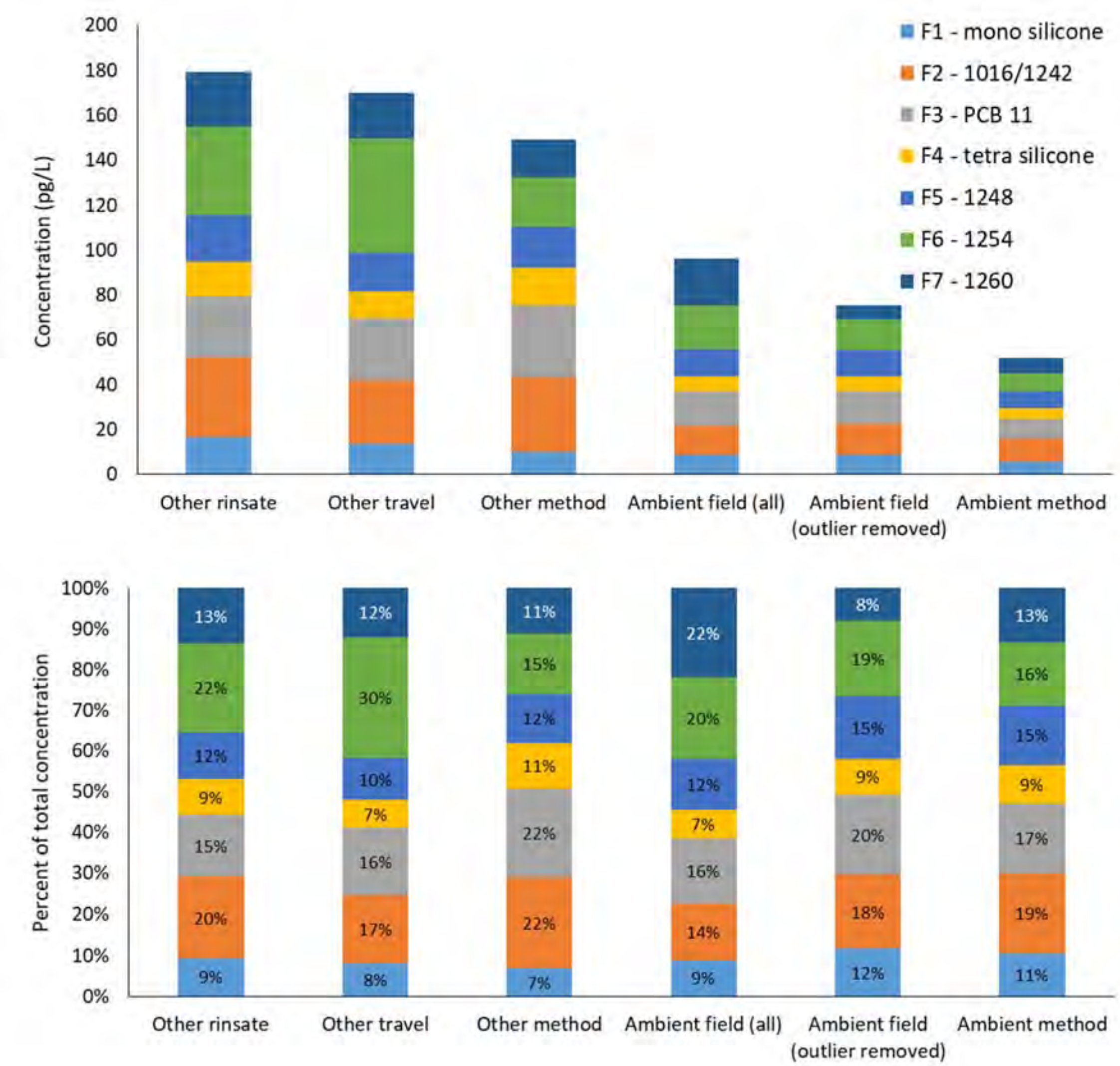

Figure S-2. Distribution of the seven factors isolated from analysis of the blank via PMF across the different types of blanks. The ambient field and ambient method blanks (i.e. the three columns to the right) were used to correct the data described in the main text. Blanks from other studies (three columns on the left) were included in the PMF model in order to increase the statistical power of the PMF analysis. These 'out of study' blanks are described above in the section "Types of blanks." In this figure, the results are presented for all ambient field blanks as well for the ambient field blanks with the exclusion of the one blank with the highest PCB concentration in the data set (Σ_{75}PCBs = 675 pg/L).

Table S-2. F-matrix of the BatchCensor68 PMF model solution

IUPAC	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
2	2.118%	0.004%	0.079%	0.000%	0.008%
4	2.665%	3.550%	0.474%	0.000%	0.095%
8	1.354%	5.467%	0.248%	0.587%	0.155%
11	68.527%	0.003%	0.001%	0.402%	0.004%
15	1.592%	3.079%	1.220%	0.201%	0.078%
16	1.689%	2.370%	0.983%	0.803%	0.011%
17	1.485%	2.699%	0.894%	0.719%	0.002%
18	3.145%	6.131%	2.211%	1.434%	0.015%
19	0.498%	1.627%	1.208%	0.000%	0.000%
20	0.789%	10.681%	8.148%	1.769%	0.002%
21	3.199%	2.666%	0.586%	0.993%	0.264%
22	0.493%	3.847%	2.836%	0.562%	0.100%
25	0.076%	0.558%	0.456%	0.170%	0.000%
26	0.129%	1.819%	1.271%	0.293%	0.000%
27	0.073%	0.652%	0.529%	0.000%	0.001%
31	0.677%	8.201%	5.880%	1.509%	0.002%
32	0.143%	1.583%	1.784%	0.122%	0.059%
37	0.857%	1.527%	1.070%	0.767%	0.264%
40	0.003%	2.436%	3.451%	1.277%	0.312%
42	0.001%	1.305%	2.079%	0.454%	0.136%
44	1.742%	1.707%	10.164%	3.307%	0.771%
45	0.929%	0.516%	2.910%	0.001%	0.242%
46	0.001%	0.403%	0.603%	0.138%	0.002%
48	0.208%	0.830%	1.063%	0.566%	0.106%
49	0.001%	3.513%	5.077%	1.483%	0.014%
50	0.006%	1.260%	1.625%	0.115%	0.025%
52	0.332%	6.608%	9.954%	5.294%	0.316%
56	0.053%	1.374%	2.139%	1.257%	0.337%
59	0.001%	0.542%	0.786%	0.193%	0.047%
60	0.052%	0.732%	1.143%	0.748%	0.191%
61	0.107%	5.024%	7.474%	6.320%	1.852%
64	0.001%	2.468%	3.621%	1.131%	0.227%
66	0.004%	3.269%	4.451%	2.346%	0.595%
77	0.182%	0.135%	0.300%	0.241%	0.379%
82	0.003%	0.007%	0.341%	0.870%	0.465%
83	0.084%	0.699%	1.176%	4.235%	2.099%
84	0.412%	0.062%	0.781%	1.957%	1.003%
85	0.150%	0.276%	0.590%	1.336%	0.731%
86	0.911%	0.002%	1.522%	5.701%	2.770%
88	0.006%	0.354%	0.536%	0.946%	0.368%
90	0.350%	0.875%	1.687%	7.973%	3.750%
92	0.132%	0.196%	0.371%	1.434%	0.653%
93	1.835%	1.518%	2.217%	5.716%	2.769%
105	0.004%	0.002%	0.657%	2.278%	2.450%
107	0.060%	0.002%	0.075%	0.453%	0.387%
110	0.094%	0.450%	1.898%	8.826%	5.256%
118	0.002%	0.002%	0.900%	6.289%	5.081%
128	0.002%	0.000%	0.000%	0.809%	1.966%
129	0.002%	0.104%	0.002%	4.237%	11.047%
132	0.366%	0.163%	0.007%	2.108%	2.384%
135	0.558%	1.313%	0.000%	1.340%	2.669%
136	0.124%	0.605%	0.000%	0.564%	0.744%
141	0.051%	0.225%	0.001%	0.938%	1.561%
146	0.198%	0.036%	0.000%	0.317%	1.650%
147	0.013%	2.199%	0.000%	3.647%	6.062%
153	0.345%	0.529%	0.000%	0.701%	10.560%
156	0.001%	0.001%	0.000%	0.503%	1.294%
158	0.001%	0.000%	0.000%	0.515%	0.970%
170	0.005%	0.001%	0.076%	0.108%	2.390%
174	0.112%	0.520%	0.001%	0.447%	2.277%
177	0.173%	0.157%	0.001%	0.278%	1.371%
179	0.191%	0.481%	0.000%	0.171%	0.900%
180	0.014%	0.002%	0.185%	0.001%	6.228%
183	0.075%	0.259%	0.001%	0.098%	2.073%
187	0.021%	0.375%	0.000%	0.002%	4.604%
194	0.053%	0.000%	0.120%	0.000%	1.412%
198	0.414%	0.000%	0.059%	0.000%	2.128%
203	0.109%	0.001%	0.077%	0.000%	1.318%

Table S-3. G matrix of the BatchCensor68 PMF model solution (concentrations in pg/L).

Sample ID	Date	Station	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
HC1-032416-1355	3/24/2016	HC1	9.86E+00	2.92E+01	6.98E+00	1.52E+01	1.95E+01
HC1-041916-1340	4/19/2016	HC1	7.34E+00	2.10E+01	5.17E+00	1.02E+01	9.69E+00
HC1-052416-1430	5/24/2016	HC1	1.09E+01	9.23E+00	2.38E+01	2.39E+01	1.74E+01
HC1-061616-0827	6/16/2016	HC1	1.80E+01	1.60E+01	8.45E+00	1.47E+01	1.33E+01
HC1-081214-1130	8/12/2014	HC1	9.47E+00	1.10E+01	6.56E+00	2.96E+01	2.42E+01
HC1-081214-1130 DUP	8/12/2014	HC1	1.45E+01	1.05E+01	1.35E+01	3.38E+01	4.73E+01
HC1-081414-1520	8/14/2014	HC1	1.23E+01	1.39E+01	7.69E+00	4.27E+01	4.02E+01
HC1-081614-1455	8/16/2014	HC1	1.44E+01	9.06E+00	1.20E+01	3.62E+01	4.39E+01
HC1-081814-1550	8/18/2014	HC1	1.27E+01	6.30E+00	1.03E+01	2.90E+01	3.17E+01
HC1-082014-1515	8/20/2014	HC1	4.80E+00	1.27E+02	4.84E+02	1.09E+03	6.09E+02
HC1-082214-1550	8/22/2014	HC1	1.48E+01	5.79E+00	1.44E+01	9.64E+01	1.47E+02
HC1-082414-1500	8/24/2014	HC1	1.08E+01	6.01E+00	6.30E+00	4.10E+01	3.88E+01
HC1-102616-1415	10/26/2016	HC1	2.32E+01	3.34E-02	6.07E+01	2.02E+02	7.02E+02
HC1-121316-1520	12/13/2016	HC1	9.19E+01	6.27E+00	4.36E+01	1.77E+01	2.31E+01
HC1-Composite	August 2014	HC1	2.23E+01	1.15E+01	8.51E+00	3.36E+01	3.91E+01
SR1-032416-1445	3/24/2016	SR1	5.78E-03	9.33E+00	2.67E+01	4.71E+01	2.83E+01
SR1-041916-1301	4/19/2016	SR1	8.42E+00	1.25E+01	2.28E+01	2.04E+01	2.10E+01
SR1-052416-1300	5/24/2016	SR1	2.84E+01	3.04E+01	5.55E+01	4.03E+01	6.07E+01
SR1-061616-0722	6/16/2016	SR1	1.88E+01	3.04E+01	3.53E+01	3.00E+01	2.47E+01
SR1-081214-0945	8/12/2014	SR1	4.70E+01	1.72E+01	3.55E+01	3.83E+01	2.61E+01
SR1-081214-0945 DUP	8/12/2014	SR1	5.16E+01	2.13E+01	4.74E+01	4.91E+01	2.88E+01
SR1-081414-1435	8/14/2014	SR1	3.90E+01	3.27E+01	3.12E+01	5.09E+01	4.32E+01
SR1-081614-1350	8/16/2014	SR1	3.42E+01	3.48E+01	3.98E+01	3.89E+01	5.63E+01
SR1-081814-1440	8/18/2014	SR1	3.40E+01	1.81E+01	3.76E+01	5.58E+01	3.67E+01
SR1-082014-1410	8/20/2014	SR1	3.38E+01	2.38E+01	4.87E+01	6.71E+01	5.69E+01
SR1-082214-1500	8/22/2014	SR1	3.10E+01	1.96E+01	4.15E+01	4.75E+01	3.24E+01
SR1-082414-1600	8/24/2014	SR1	3.36E+01	1.97E+01	3.52E+01	4.58E+01	2.90E+01
SR1-102616-1320	10/26/2016	SR1	1.67E+01	5.26E-01	5.08E+01	3.20E+01	4.31E+01
SR1-102616-1320 DUP	10/26/2016	SR1	1.34E+01	3.35E+00	4.67E+01	2.65E+01	2.85E+01
SR1-121316-1420	12/13/2016	SR1	7.97E+01	9.79E+00	5.85E+01	2.28E+01	2.37E+01
SR12-081214-1545	8/12/2014	SR12	8.38E+00	1.07E+01	5.21E+00	2.30E+01	2.08E+01
SR12-081414-1015	8/14/2014	SR12	9.98E+00	5.06E+00	1.31E+01	1.78E+01	2.10E+01
SR12-081614-0845	8/16/2014	SR12	5.59E+00	1.22E+01	6.58E-03	1.15E+01	2.40E+01
SR12-081814-0945	8/18/2014	SR12	9.57E+00	9.81E+00	8.15E+00	2.61E+01	2.01E+01
SR12-082014-0945	8/20/2014	SR12	1.22E+01	6.05E+00	1.28E+01	1.70E+01	1.62E+01
SR12-082214-0935	8/22/2014	SR12	7.74E+00	2.03E-01	4.21E-03	8.89E+00	3.93E+01
SR12-082414-1030	8/24/2014	SR12	9.13E+00	1.06E-02	5.70E+00	3.18E+01	2.15E+01
SR12-082414-1030 DUP	8/24/2014	SR12	9.84E+00	5.60E-01	2.52E-03	3.48E+00	7.74E-01
SR12-Composite	August 2014	SR12	1.70E+01	1.97E-01	1.85E+01	8.25E+01	1.16E+02
SR15-032416-0930	3/24/2016	SR15	1.87E-02	7.63E-03	6.90E+00	1.08E+01	1.26E+01
SR15-032416-0930 DUP	3/24/2016	SR15	3.85E-01	7.59E-03	9.21E+00	3.66E+00	1.63E+01
SR15-041916-0825	4/19/2016	SR15	8.18E+00	7.71E+00	2.87E+00	4.55E+00	1.12E+01
SR15-052416-0835	5/24/2016	SR15	1.99E+01	1.59E+01	2.87E+01	1.83E+01	1.39E+01
SR15-061616-1133	6/16/2016	SR15	1.97E-01	1.41E-02	4.38E-03	1.55E+01	1.40E+01
SR15-081214-1425	8/12/2014	SR15	6.15E+00	2.68E+00	5.11E+00	1.56E+01	1.06E+01
SR15-081414-0835	8/14/2014	SR15	7.12E+00	2.68E+00	1.12E+01	1.79E+01	2.27E+01
SR15-081614-0740	8/16/2014	SR15	5.70E-01	1.81E+00	1.02E+01	1.48E+01	1.51E+01
SR15-081814-0840	8/18/2014	SR15	7.43E+00	1.30E+01	1.45E-02	1.76E+01	1.01E+01
SR15-082014-0820	8/20/2014	SR15	9.49E+00	5.28E+00	9.48E+00	1.09E+01	1.07E+01
SR15-082214-0830	8/22/2014	SR15	9.40E+00	2.82E+00	2.67E-03	6.33E-01	8.39E-01
SR15-082314-1130	8/23/2014	SR15	7.62E+00	1.66E+00	3.35E-03	7.20E-01	7.76E-01
SR15-102616-0900	10/26/2016	SR15	4.30E-02	1.48E-02	6.85E+00	1.24E+01	1.83E+01
SR15-Composite	August 2014	SR15	3.77E-01	4.27E+00	2.22E+00	1.80E+01	1.56E+00
SR1-Composite	August 2014	SR1	3.56E+01	1.81E+01	2.91E+01	4.16E+01	2.95E+01
SR3-032416-1325	3/24/2016	SR3	8.70E-03	1.07E+01	1.81E+01	2.80E+01	2.09E+01
SR3-041916-1425	4/19/2016	SR3	8.40E+00	9.75E+00	2.37E+01	1.36E+01	2.25E+01
SR3-052416-1400	5/24/2016	SR3	1.49E+01	2.54E+01	2.74E+01	3.14E+01	3.16E+01
SR3-061616-0849	6/16/2016	SR3	1.26E+01	2.43E+01	4.85E+01	1.52E+01	2.86E+01
SR3-061616-0849 DUP		SR3	1.22E+01	1.94E+01	5.73E+01	1.60E+01	2.48E+01
SR3-081214-1225	8/12/2014	SR3	2.76E+01	4.34E+01	3.24E+01	4.68E+01	2.51E+01
SR3-081414-1600	8/14/2014	SR3	2.91E+01	5.37E+01	3.93E+01	3.82E+01	2.99E+01
SR3-081414-1600 DUP	8/14/2014	SR3	2.57E+01	3.50E+01	3.54E+01	3.70E+01	2.71E+01
SR3-081614-1545	8/16/2014	SR3	3.63E+01	4.13E+01	5.03E+01	1.02E+02	7.33E+01
SR3-081814-1635	8/18/2014	SR3	3.03E+01	3.82E+01	4.90E+01	4.88E+01	4.19E+01
SR3-081815-1915	8/18/2015	SR3	2.37E+01	2.99E+01	4.13E+01	1.34E+02	3.44E+01
SR3-081915-0821	8/19/2015	SR3	2.66E+01	1.96E+01	3.92E+01	8.32E+01	4.67E+01
SR3-082014-1550	8/20/2014	SR3	1.88E+01	4.13E+01	5.49E+01	4.95E+01	3.14E+01
SR3-082015-1500	8/20/2015	SR3	4.51E+01	5.46E+01	4.31E+01	3.82E+01	4.11E+01
SR3-082115-0853	8/21/2015	SR3	3.63E+01	5.18E+01	4.23E+01	4.81E+01	3.25E+01
SR3-082214-1620	8/22/2014	SR3	2.13E+01	3.70E+01	5.35E+01	1.53E+02	1.23E+02
SR3-082215-1355	8/22/2015	SR3	4.47E+01	4.89E+01	5.25E+01	5.25E+01	3.17E+01
SR3-082414-1430	8/24/2014	SR3	2.04E+01	3.24E+01	3.92E+01	4.76E+01	2.83E+01
SR3-102616-1500	10/26/2016	SR3	2.39E+01	8.77E-03	6.94E+01	2.55E+01	1.04E+02
SR3-Composite	August 2014	SR3	4.53E+01	6.24E+01	1.61E+02	7.06E+01	7.64E+00

The first portion of the sample ID indicates the location, the second portion indicates the date of sample collection, and the third portion indicates the time of day of collection.

Samples labeled 'composite' were composites of all samples collected at that location during the 2015 sampling event. Samples labeled 'DUP' are duplicates.

Highest concentrations are in red, lowest in green.

Table S-3 continued

Sample ID	Date	Station	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
SR4-032416-1145	3/24/2016	SR4	1.18E-01	1.05E+01	2.58E+01	1.15E+01	3.88E+01
SR4-041916-1030	4/19/2016	SR4	8.96E+00	1.33E+01	2.20E+01	5.20E+00	4.58E+01
SR4-052416-1030	5/24/2016	SR4	2.84E+01	2.54E+01	4.64E+01	2.46E+01	2.16E+01
SR4-052416-1040 DUP	5/24/2016	SR4	1.16E+01	1.92E+01	3.17E+01	2.28E+01	2.14E+01
SR4-061616-0945	6/16/2016	SR4	1.28E+01	1.46E+01	6.69E+01	1.87E+01	2.64E+01
SR4-081314-1805	8/13/2014	SR4	1.94E+01	4.39E+01	4.25E+01	1.87E+01	3.92E+01
SR4-081414-1645	8/14/2014	SR4	1.72E+01	5.79E+01	5.18E+01	1.08E-02	7.89E+01
SR4-081614-1230	8/16/2014	SR4	1.56E+01	5.18E+01	4.36E+01	1.16E+01	2.78E+01
SR4-081814-1240	8/18/2014	SR4	1.44E+01	5.33E+01	5.44E+01	1.99E+01	2.15E+01
SR4-081814-1240 DUP	8/18/2014	Rep	1.58E+01	4.13E+01	4.57E+01	1.24E+01	1.66E+01
SR4-081815-1826	8/18/2015	SR4	3.34E+01	1.50E+01	7.39E+01	1.01E+02	2.67E+01
SR4-081915-0928	8/19/2015	SR4	3.41E+01	7.20E+00	5.86E+01	1.24E+01	1.25E+02
SR4-082014-1220	8/20/2014	SR4	1.59E+01	6.77E+01	7.96E+01	2.00E+01	3.01E+01
SR4-082015-1410	8/20/2015	SR4	3.65E+01	5.10E+01	4.39E+01	1.70E+01	2.14E+01
SR4-082115-0949	8/21/2015	SR4	3.20E+01	6.24E+01	5.01E+01	2.79E+01	3.35E+01
SR4-082214-1345	8/22/2014	SR4	1.25E+01	4.47E+01	5.33E+01	1.72E+01	1.85E+01
SR4-082215-1127	8/22/2015	SR4	4.35E+01	5.02E+01	5.38E+01	1.68E+01	2.70E+01
SR4-082414-1305	8/24/2014	SR4	1.57E+01	4.10E+01	4.58E+01	1.11E+01	1.21E+01
SR4-102616-1120	10/26/2016	SR4	1.98E+01	6.90E-03	6.27E+01	2.69E+01	5.61E+01
SR4-121316-1125	12/13/2016	SR4	8.70E+01	4.83E+00	6.18E+01	1.45E+01	2.64E+01
SR4-Composite	August 2014	SR4	5.04E+01	9.32E+01	6.16E+01	3.56E+01	1.91E+01
SR7-032416-1055	3/24/2016	SR7	4.23E-02	6.15E+00	4.10E+01	5.92E+00	1.96E+01
SR7-052416-0950	5/24/2016	SR7	2.55E+01	2.56E+01	6.34E+01	3.35E+01	2.01E+01
SR7-061616-1025	6/16/2016	SR7	8.64E+00	5.12E-02	1.05E+02	3.48E+00	1.49E+01
SR7-081214-1805	8/12/2014	SR7	7.18E+00	5.44E+00	1.35E+02	1.62E+01	1.88E+01
SR7-081414-1800	8/14/2014	SR7	6.85E+00	1.99E+01	1.03E+02	7.27E+00	5.11E+00
SR7-081614-1040	8/16/2014	SR7	7.27E+00	1.27E+01	1.43E+02	5.43E+00	1.68E+01
SR7-081814-1130	8/18/2014	SR7	7.81E+00	3.59E-02	3.14E+02	6.37E+01	1.95E+01
SR7-081815-1650	8/18/2015	SR7	4.70E-03	4.55E+01	1.21E+02	6.33E+01	4.17E-03
SR7-081915-1026	8/19/2015	SR7	1.44E-03	3.75E+01	1.02E+02	2.94E+01	1.51E+01
SR7-081915-1026 DUP	8/19/2015	SR7	1.87E+01	3.31E+01	1.04E+02	6.37E+00	1.06E+01
SR7-082014-1145	8/20/2014	SR7	6.70E+00	1.91E+01	1.30E+02	7.39E+00	1.41E+01
SR7-082014-1145 DUP	8/20/2014	Rep	6.75E+00	2.34E+01	1.35E+02	5.92E+00	1.64E+01
SR7-082015-1130	8/20/2015	SR7	8.81E-02	3.91E+01	8.85E+01	1.04E+01	7.02E+00
SR7-082115-1045	8/21/2015	SR7	1.10E-02	3.55E+01	9.83E+01	2.42E+01	1.70E-03
SR7-082214-1205	8/22/2014	SR7	8.98E+00	9.14E+00	1.12E+02	3.26E+00	3.59E-03
SR7-082215-0935	8/22/2015	SR7	2.04E+01	2.60E+01	1.31E+02	2.69E+01	2.04E-03
SR7-082414-1215	8/24/2014	SR7	5.36E+00	1.25E+01	1.27E+02	9.55E-01	4.82E-03
SR7-102616-1025	10/26/2016	SR7	9.58E-03	2.24E-02	5.20E+01	1.38E+01	2.03E+01
SR7-121316-1020	12/13/2016	SR7	6.02E+01	1.54E-02	1.05E+02	6.16E+01	4.14E+01
SR7-Composite	August 2014	SR7	2.41E+01	3.91E+01	1.10E+02	1.83E-03	5.81E-03
SR8a-081815-1019	8/18/2015	SR8	5.54E-03	2.11E+01	5.01E+00	5.28E+01	1.35E+02
SR8a-081915-1330	8/19/2015	SR8	1.22E-01	1.59E+01	1.99E+01	2.71E+01	1.89E+01
SR8a-082015-0848	8/20/2015	SR8	1.72E+01	1.31E+01	1.49E+01	1.20E+01	1.32E+01
SR8a-082115-1305	8/21/2015	SR8	3.78E-01	7.61E+00	1.22E+01	4.56E+01	3.17E+00
SR8a-082115-1305 DUP	8/21/2015	SR8a	2.29E+01	7.53E+00	1.36E+01	5.78E-01	3.90E-03
SR8a-082215-1525	8/22/2015	SR8	1.89E+01	9.31E+00	9.37E+00	1.89E+01	2.50E-03
SR8a-Composite	8/22/2015	SR8	1.97E+01	4.06E-03	3.59E-03	5.90E-03	3.39E-01
SR9-041916-0915	4/19/2016	SR9	6.64E+00	5.04E+00	4.42E+00	4.66E+00	1.53E+01
SR9-041916-0916 DUP	4/19/2016	SR9	8.07E+00	3.11E+00	8.55E+00	7.81E+00	1.59E+01
SR9-081214-1720	8/12/2014	SR9	8.35E+00	3.30E+00	6.95E+00	1.58E+01	1.57E+01
SR9-081414-1140	8/14/2014	SR9	1.15E+01	8.76E+00	1.12E+01	1.54E+01	2.04E+01
SR9-081614-0940	8/16/2014	SR9	7.71E+00	5.24E+00	8.80E+00	1.24E+01	1.19E+01
SR9-081814-1045	8/18/2014	SR9	8.28E+00	1.61E+01	9.87E+00	1.46E+01	1.54E+01
SR9-081815-0832	8/18/2015	SR9	2.17E-01	1.48E+01	1.04E+01	3.74E+01	1.07E-02
SR9-081915-1450	8/19/2015	SR9	2.16E+01	1.26E+01	1.21E+01	1.11E+01	1.46E+01
SR9-082014-1045	8/20/2014	SR9	1.34E+01	6.44E+00	1.04E+01	1.08E+01	1.40E+01
SR9-082015-0750	8/20/2015	SR9	2.12E+01	1.74E+01	1.74E+01	1.13E+01	1.55E+01
SR9-082115-1429	8/21/2015	SR9	2.05E+01	4.71E-03	6.36E-03	1.08E+02	3.18E+01
SR9-082214-1030	8/22/2014	SR9	8.05E+00	1.24E+00	4.36E-03	4.65E-01	8.20E-01
SR9-082214-1030 DUP	8/22/2014	Rep	8.43E+00	1.01E-02	2.09E-03	5.82E+00	5.22E+01
SR9-082215-0733	8/22/2015	SR9	2.99E+01	1.26E+01	2.04E+01	1.23E+01	3.18E+01
SR9-082215-0733 DUP	8/22/2015	SR9	2.87E+01	1.71E+00	2.32E+01	4.82E+01	3.15E+01
SR9-082414-1125	8/24/2014	SR9	9.45E+00	1.45E+00	5.39E-03	1.05E+00	9.14E-01
SR9-Composite	August 2014	SR9	3.53E+01	5.22E-03	2.67E-03	3.33E-03	3.99E-01

The first portion of the sample ID indicates the location, the second portion indicates the date of sample collection, and the third portion indicates the time of day of collection.

Samples labeled 'composite' were composites of all samples collected at that location during the 2015 sampling event. Samples labeled 'DUP' are duplicates.

Highest concentrations are in red, lowest in green.

REFERENCES

Antweiler, R. C. 2015. "Evaluation of Statistical Treatments of Left-Censored Environmental Data Using Coincident Uncensored Data Sets. II. Group Comparisons." *Environmental Science & Technology* 49 (22):13439-46. doi: 10.1021/acs.est.5b02385.

Haslauer, C. P., J. R. Meyer, A. Bardossy, and B. L. Parker. 2017. "Estimating a Representative Value and Proportion of True Zeros for Censored Analytical Data with Applications to Contaminated Site Assessment." *Environmental Science & Technology* 51 (13):7502-10. doi: 10.1021/acs.est.6b05385.

Huang, L. D., K. Bradshaw, J. Grosskleg, and S. D. Siciliano. 2019. "Assessing Space, Time, and Remediation Contribution to Soil Pollutant Variation near the Detection Limit Using Hurdle Models to Account for a Large Proportion of Nondetectable Results." *Environmental Science & Technology* 53 (12):6824-33. doi: 10.1021/acs.est.8b07110.

LimnoTech. 2014a. "Quality Assurance Project Plan: Spokane River Toxics Reduction Strategy Study." In.: Prepared for the Spokane River Regional Toxics Task Force.

———. 2014b. "Sampling & Analysis Plan Spokane River Toxics Reduction Strategy Study." In, 65 pp. Spokane, WA: Spokane River Regional Toxics Task Force.

Norris, G., K. Katie Wade, P. Zahn, S. Brown, P. Paatero, S. Eberly, and C. Foley. 2009. "Guidance Document for PMF Applications with the Multilinear Engine." In. Research Triangle Park, NC: U.S. EPA.

Polissar, V. A., and P. H. Hopke. 2001. "Atmospheric Aerosol over Vermont: Chemical Composition and Sources." *Environ. Sci. Technol.* 35:4604-21.

Reff, A., S. I. Eberly, and P. V. Bhave. 2007. "Receptor modeling of ambient particulate matter data using positive matrix factorization: Review of existing methods." *Journal of the Air & Waste Management Association* 57 (2):146-54.

Rodenburg, L. A., S. Du, D. E. Fennell, and G. J. Cavallo. 2010. "Evidence for Widespread Dechlorination of Polychlorinated Biphenyls in Groundwater, Landfills, and Wastewater Collection Systems." *Environ. Sci. Technol.* 44:7534-40. doi: 10.1021/es1019564.

Rodenburg, L. A., and D. K. Ralston. 2017. "Historical sources of polychlorinated biphenyls to the sediment of the New York/New Jersey Harbor." *Chemosphere* 169:450-9.

Rodenburg, Lisa A., and Damon A. Delistraty. 2019. "Alterations in fingerprints of polychlorinated biphenyls in benthic biota at the Portland Harbor Superfund Site (Oregon, USA) suggest metabolism." *Chemosphere* 223:74-82.

Rodenburg, Lisa A., and Qingyu Meng. 2013. "Source Apportionment of Polychlorinated Biphenyls in Chicago Air from 1996 to 2007." *Environmental Science & Technology* 47 (8):3774-80. doi: 10.1021/es305024p.

Spokane County Water Reclamantion. 2015. "Spokane County Regional Water Reclamation Facility NPDES Permit WA-0093317 Revision 3 Quality Assurance Project Plan." In, 146 pp. Spokane, WA.

U. S. EPA. 2010. "Method 1668C: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS." In. Washington, DC,: United States Environmental Protection Agency.